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ELEMENTARY
STUDIES IN CHEMISTRY

BY

JOSEPH TORREY, Jr.
Instructor in Harvard University

NEW YORK
HENRY HOLT AND COMPANY
1899

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DEDICATED TO MY STUDENTS,
PAST AND PRESENT.

PREFACE.

CHEMISTRY has had a varied history in its comparatively short career as an educational factor; but it has never yet commanded universal respect, nor has it, I think, ever been authoritatively recognized as equal in educational value to Greek, Latin, and mathematics—the standards by which, whether we like it or not, all educational subjects have been measured in the past and will be measured for some time to come.

The beneficial effects of chemistry as an element of variety, or as a sort of counter-irritant, have always been recognized; but this is not the same thing as according it educational value. When all is said and done, teachers and students alike recognize the fact that a year's work in chemistry as given in the average secondary school stands for a decidedly smaller outlay of energy than a year of Greek, Latin, or mathematics, and the feeling is a perfectly natural and logical one that the results measured in terms of mental discipline vary in about the same ratio.

If these statements be accepted as substantially true, as they probably will be, the question naturally arises whether this state of things is inevitable. Is there anything in Greek or in any other subject which gives it a position to which chemistry cannot attain?

I believe not. I am most decidedly of the opinion that two subjects upon which the same amount of scholarly energy has been expended, and expended with reference to the needs of the elementary student, have necessarily the same educational value. In case of chemistry this condition is not met. In the first place the problem is a somewhat complicated one, and in the second place it has not been studied long enough or carefully enough. Without going into ancient history too far, it may be said that the main difficulty is and always has been that the subject has been handled too gingerly. One would be tempted to think on examining some proposed courses that there was something weird and uncanny about the subject, and that students should only be allowed to peek at it through a very small crack indeed. Moreover, chemistry has suffered from the irrepressible wave of laboratory madness which has swept over the whole educational world. Laboratory work has been carried far beyond its limits and things have been expected of it which it never did and never can do. The elements of systematic and careful instruction, study, and training in accuracy of observation and statement which were and are the strong points of the older subjects have been neglected, and nothing equivalent has been put in their place.

Still further. Starting with the eminently reasonable proposition that scientific study should train the reasoning powers, we have run that same proposition far into the ground. Nothing too severe can be said against the mechanical and demoralizing system of note-books with "operation," "observation," and "inference" headings. They are wholesale breeders of dishonest and superficial work. It has fallen to the writer's lot to read very many such; and they have been one continuous round of observations either spurious or inaccurate and of inferences unwarranted.

The first thing and the hardest to teach a student is to use his senses, i.e. to observe accurately; and in my opinion this should be accomplished even if everything else has to go. It is of no avail to reason until there is something to reason about. When the facts brought out by an experiment have been established on a respectable basis and stated clearly and completely in the notes, the bearing of those facts will generally reveal itself. When the student gets to a point where he is encouraged to put two and two together, he needs example—and that is where a much neglected duty of the teacher comes in. He ought to take some pieces of work to the lecture-table, carry out the experiments, and then set in order the facts, point out what they suggest, and draw any conclusions that can legitimately be drawn—all in his very best style. It is a valuable exercise for the teacher, and its effect upon a class is decided and positive.

This book contains material enough for a thorough course in elementary chemical theory and for some study of individual elements. It is hardly probable that all the work herein contained can be done in one year; but it has been thought best to make it fairly comprehensive, because considerable reading can be profitably done by a class toward the end of the year, and because it is often desirable to vary the line of study from year to year.

The time required to do successful work is at least five and preferably six hours per week, of which one third ought to be devoted to reading with the class and discussion of results.

Students entering upon the study of chemistry ought to have behind them elementary physics, geometry, and algebra. There can be no sound knowledge of the subject without them. The first ten lectures and exercises deal with matters which ought to be particularly well in hand. If the teacher knows that they are, the work may begin at lecture 11. There is distinctly some loss in omitting these first exercises unless the principles, methods, and conceptions there brought out have been dealt with elsewhere with equal thoroughness.

It has not been thought best to include any systematic work in the line of qualitative analysis. It is believed that the same results can be reached by the working out of simple problems involving separations, in the laboratory. Qualitative analysis is very easily overdone.

It is probable that many inaccuracies and mistakes of one kind or another will emerge as the book comes under scrutiny. It has been written in a very disjointed fashion, during the last two years, and while the proof has been read as carefully as possible, it is likely to need correction in many particulars. I shall be grateful to any who will call my attention to such inaccuracies as may be noticed.

I hope the language will prove clear: this point has been kept constantly in mind. Professor Arlo Bates has been so kind as to read the entire work in proof; and his suggestions and criticisms have been of the greatest assistance. My brother, Mr. E. B. Torrey, has furnished the drawings from which the cuts are made. Formal acknowledgment is a very inadequate expression of my gratitude for these services.

J. T.

HARVARD UNIVERSITY,
May 24, 1899.

ELEMENTARY STUDIES IN CHEMISTRY

LECTURE 1.

THE science of chemistry is comparatively young. It is true that many of its facts have been matters of human knowledge and interest from a very early period; but the knowledge was for a long time exceedingly vague, and the scattered facts only very imperfectly understood. Most of the early investigation was connected with the search after a method of changing the common metals into gold. In Egypt, especially, we find great attention paid to this problem even before the time of Christ. Later, from the eighth century on, we see the ideas and methods of the Egyptian experimenters carried by the Arabs into Spain; from which country the "Alchemists" then spread gradually through the whole of Europe; their number constantly increasing, and their crude ideas and methods receiving constant improvement. But progress was slow, and it is not until the early part of the present century that we begin to see established the principles and methods which have brought order out of confusion, and elevated chemistry to the rank of a science.

The word "science" implies two things: first, that a large number of carefully attested facts have been accumulated; and second, that there has been some attempt to classify and generalize these facts. As long as any science continues to advance, both these processes must go on, though not always at the same rate. There will be periods when facts are accumulated faster than they can be made available; with the result that valuable and suggestive material sometimes has to wait a long time before it is used. On the other hand, there occasionally come periods of great activity in the other direction; when great accumulations of material crystallize into generalizations or *laws*, under the touch of master hands. Any one who wishes to advance scientific knowledge by his own investigations, must either contribute to its wealth of facts, or else set in order and arrange existing material. Neither of these tasks can be counted a light one.

In beginning our study of chemistry it is necessary for us to enter, so far as possible, into the spirit of scientific investigation. It is true that we shall merely tread where others have trod; but we shall at least see how facts are established, and how we are led by a study of these facts to the great generalizations which are the backbone of the modern science of chemistry. This experience will tend to increase our respect for the science, and for truth in general. Let us therefore confine ourselves, for a while, to such work as will give us an insight into some of the principles which must always be in the mind of any one who undertakes to add to the existing mass of scientific fact.

In chemistry, or in any physical science, the facts with which we deal are either *qualitative* or *quantitative* in their nature. If, for example, we satisfy ourselves that a certain dish contains water, our knowledge is merely *qualitative*. If, however, we ascertain exactly how much water there is in the vessel, both by measure and by weight, we have a *quantitative* knowledge of the matter. The history of the physical sciences shows that in the early days people interested themselves mainly in qualitative facts; but it is worthy of note that no great progress was made until the time when emphasis was laid on careful quantitative investigation. It is in this latter field, then, that we come most speedily into contact with the methods and principles which are characteristic of scientific progress. Accordingly, our first work will be quantitative, and will consist in finding the weight of a given volume of water.

In measuring, it is of course necessary to have a standard of measurement. We ordinarily express the length of a stick or any similar object in feet and inches, the weight of a body in pounds and ounces, and so on; but for our measurements we shall use a unit of length which is different from any of those just mentioned, and which is very convenient, for reasons which will appear hereafter. It is called the *centimeter*, and is about $\frac{2}{5}$ of an inch. We measure areas in *square centimeters*, and volumes in *cubic centimeters*. Strictly speaking, the unit of length in this so-called *metric system* is the *meter*, which is a little more than a yard, the centimeter being the one hundredth part of a meter. For such measurements as we are to make, however, the centimeter will be the more convenient unit.

In the same way we use a unit of weight which is different from the pound, ounce, or grain. It is the *gram*, which is equal to about 15 of our grains, and is therefore about $\frac{1}{23}$ of an ounce. One thousand of these grams make 1 *kilogram*, which is a weight useful for weighings which would ordinarily be expressed in pounds. For the present all our weights will be recorded in grams and decimal fractions of a gram.

When we enter upon a problem like the present one, it is not to be expected that we shall, at the first attempt, reach a result which represents the greatest accuracy we can attain with the means at our disposal. On the contrary, experience shows that this is almost never the case, and that the first trial serves mainly as a sort of training for subsequent attempts.

From this point of view the following method will be a good one to begin with. It seems to promise well, and will give us a chance to get acquainted with the balance, weights, and rule.

LABORATORY WORK.

Take a small hollow cylinder of tin, weighted with shot, so that it will sink under water. Attach it *neatly* to one pan of the balance by means of a wire stirrup and a piece of thread as in Fig. 1. Counterpoise the cylinder as accurately as possible with fragments of metal, shot, or sand.

Next arrange the cylinder so that it may swing, completely immersed, throughout its entire path of motion, in water contained in a pint fruit-jar. Add weights to the lighter pan till the lost weight is *exactly* restored. This loss in weight represents the weight of a volume of water equal to the volume of the cylinder. We can easily see that this must be so from the following considerations.

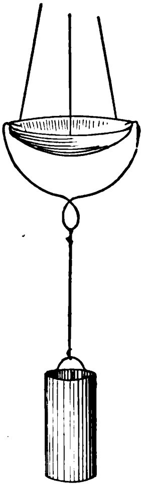

FIG. 1.

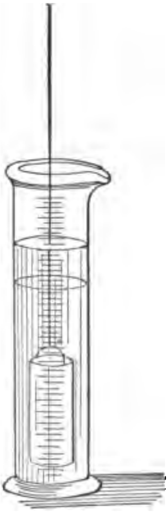

FIG. 2.

Here is a tall narrow glass vessel containing water (Fig. 2). When you immerse the cylinder in the water, the water is pushed aside and forced to go somewhere else. Now there is only one direction in which it is free to go, and that is upward; so all the water that is pushed aside by the cylinder must be *lifted*. It is easy to see how much water is pushed aside. It must be the cylinder's own volume of water. Therefore in sinking under water the cylinder has to *lift its own volume of water*. The force that sinks it is its weight, i.e., the action of gravity upon it. It is now clear that a certain amount of weight must be used up in the operation of sinking, and that the amount of weight thus lost will be the weight of the cylinder's own volume of water.

If now we can determine accurately the volume of the cylinder in cubic centimeters, we shall have ascertained—

1. The weight of the cylinder's own volume of water;
2. The volume of this water;

from which we can easily calculate the weight of one cubic centimeter of water, which is the result desired.

A convenient method of measuring the cylinder's volume is the following: Take a narrow strip of paper (about ½ centimeter wide) and cut it to such a length that it will just reach round the cylinder. Measure this strip in centimeters and we have the circumference, which is one dimension we need. The other dimension needed is the height, which can be directly measured by the rule.*

The volume of the cylinder can now be calculated by the formula $V = \frac{C^2h}{4\pi}$; V being the volume, C the circumference as measured, and h the weight as measured, while $\pi = 3.1416$.

Having thus obtained the volume of the cylinder we divide the weight of the displaced water by it, and our first determination, of the weight of one cubic centimeter of water, is at an end.

---

* It is well to cut several successive strips and measure them with all possible care, recording the results. The mean of these measurements will be a safe value to use.

LECTURE 2.

WE have now solved the problem proposed, by one method. There remains the important task of reviewing our work, in order to see whether the method employed turns out to be a well-chosen one.

One criticism which suggests itself is that the method involves a rather large number of operations. Other things being equal, a simpler one would be better. A far more serious objection is that we have virtually assumed our cylinder to be a perfect one. That is, we have assumed its circumference to be a true circle, and its height to be everywhere the same. Nevertheless the eye easily detects lack of truth in the shape of the base, and the rule shows small differences of height. Moreover, in many cases the two bases of the cylinder are not equal in circumference.

But in our calculation we have used a formula which applies only to a perfect cylinder; the general result will be that the volume as calculated from our measurements will not represent the real volume. Will it not be better to devise a method which will be free from this particular source of error?

The following method meets the requirement, though it, in turn, may be found to have its disadvantages. It is, like the first method, a means of learning from experience.

Partially fill with water a cylindrical glass vessel graduated in cubic centimeters and wide enough to admit the metal cylinder. Read the level at which the water stands. In making such readings the eye must be situated similarly with reference to the liquid level at each reading, and we must select some line in the curved surface, or *meniscus*, which is sharp and clear enough to be placed with accuracy. The best method is to bring the curve of the meniscus tangent to the graduation line at each reading, the graduate being held in front of a dark surface to make the lines show more clearly. (See Fig. 3.)

Having carefully recorded the level, put in the cylinder and let it sink under the water, taking care to dislodge all air-bubbles from the sides and bottom of the cylinder. Take a second reading: the difference between the two is evidently the volume of the cylinder in cubic centimeters.

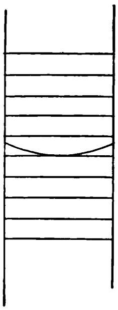
FIG. 3.

Now although we have here eliminated all question as to the cylinder's shape, it can be seen in advance that this second method leaves something to be desired. The glass vessel is graduated only to *cubic centimeters;* and, moreover, the graduation may not be the same in all parts of the scale. This last difficulty can be partially met by making several measurements with the water at different heights in the graduate, when an average will give a more truthful result than any single one. The fact remains, however, that it is almost impossible for an inexperienced eye to divide one of these cubic-centimeter divisions into more than three equal parts; so that we can only be sure of our measurements within half a cubic centimeter or so. Of course it may sometimes happen that the two levels will both fall on graduation lines and not between them. In this case the result will be a little more satisfactory. If the level comes between two graduation lines, we can get at the true reading as follows:

Make a "pipette" from tubing of about 4 mm. internal diameter. Its length should be about eight inches (Fig. 4). Make a file-scratch at *A*. Suck water into the pipette to the point *A*, then allow it to run out slowly into the graduated cylinder until just one cubic centimeter has been added to the water in the cylinder. Make another file-scratch at *B*, where the water-level now stands, and divide the distance *AB* into ten equal parts, marking the divisions by file scratches. The pipette can now be used to determine just the volume displaced by the cylinder when it sinks under water. Suppose, for example, that the level in the graduate stands as shown in Fig. 5, where the lowest dip of the meniscus falls between 80 c.c. and 81 c.c. To find how many tenths over 80 the real value is, fill the pipette carefully to *A*, then slowly run water into the graduate until the level stands at 81. Suppose it takes four tenths of a cubic centimeter, then the water originally stood at 80.6. In the same way any similar case can be managed.

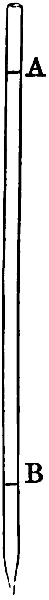

FIG. 4.

If the pipette is carefully made, the measurements of the cylinder's volume by this method become trustworthy within one or two tenths of a cubic centimeter; and this is considerable advance in precision.

We have now made use of two quite different methods for measuring the cylinder's volume. The following method is like the preceding one in that it does not depend upon the shape of the cylinder. It is, however, somewhat different in principle.

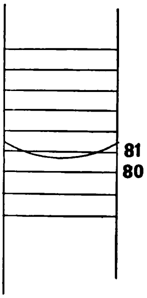

FIG. 5.

The arrangement of apparatus is shown in Fig. 6. The cylinder is attached to the balance-pan as shown. In each pan is a small beaker. Begin by bringing the whole to *perfect* equilibrium by putting small pieces of sheet lead, shot, sand, or any convenient substance into the right-hand beaker.* When this has been done place a suitable jar of water (a pint fruit-jar is convenient) so that the cylinder can swing freely up and down when immersed in the water. The cylinder when immersed loses an amount of weight equal to the weight of its own volume of water, as we have seen; and if we add water to the beaker in the left-hand pan until exact equilibrium is restored, we can easily see that the volume of water required to do this will just equal the volume of the cylinder. Now since the cylinder does not, in this case, have to be immersed in the measuring-tube, it is possible to use a narrower and consequently more delicately graduated tube, called a *burette* (see Fig. 7). With this instrument we can measure the amount of water added, to the tenth of a cubic centimeter. In adding the water to the beaker in the balance-pan, begin by adding within about half a cubic centimeter of what your former results have indicated as the volume. Then add the remainder very

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* Always use a counterpoise when possible. Avoid the uncertainty involved in reading weights.

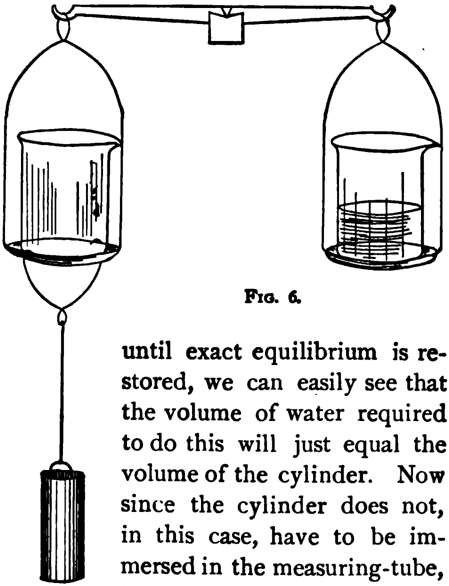

FIG. 6.

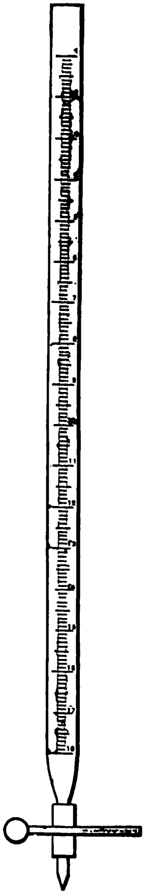

FIG. 7.

slowly and carefully, a very small drop at a time, until perfect equilibrium is reached.*

The balance should be sensitive to $\frac{1}{100}$ of a gram, and the use of the burette enables us to measure the volume within at least $\frac{1}{10}$ of a cubic centimeter; so that the results are well worth considering, even in comparison with the preceding simple and direct method of measuring the displaced water.†

---

* The work described in this lecture should now be carried out in the laboratory.

† The weight of the displaced water would be found just as in the preceding method.

LECTURE 3.

In all three of the methods thus far employed for determining the weight of one cubic centimeter of water we have ascertained the *weight* of the displaced water by the same method; but the *volume* of the displaced water has been determined by three independent methods, in the first of which, the measuring instrument was the rule; in the second, the glass graduate; and in the third, the balance and burette.

This last method is of special interest, for by a slight rearrangement of its details we can determine both the volume and the weight of the displaced water, without once detaching the cylinder from the balance-pan.

LABORATORY WORK.

Counterpoise the cylinder, having the beaker in the cylinder-pan as before (see Fig. 6).

Immerse the cylinder and add weights to restore equilibrium. (What does the weight added represent?)

Remove the weights and restore equilibrium by adding water from the burette. (What does this give?)

A good form in which to put the final results of your work is given below.

DETERMINATION OF THE WEIGHT OF ONE CUBIC CENTIMETER OF WATER.

A. Weight of Displaced Water.

Cylinder counterpoised in air, then immersed in water
Weights added to restore equilibrium = ...
Weight of displaced water ....

B. VOLUME OF DISPLACED WATER.

$\text{Vol.} = \frac{C}{4\pi}$

Log $c \times 2$ = ...

Log 4π = ...

Log vol. = ...

∴ vol. = ...

1. By Measurement of Cylinder.

	Circumference.	Height.
1.	....	....
2.	....	....
3.	....	....
Mean	......	....

2. Graduate Method. (Direct.)

Level of water without cylinder............

" " " with cylinder..............

Volume of displaced water = ...

3. Counterpoise and Burette Method.

a. Weights added to restore equilibrium = ...

b. Volume of water added from burette to restore equilibrium =.......

CALCULATION OF RESULTS FROM THE THREE METHODS.

	I.	II.	III.	IV.
Log wt. of displaced water	....	....	....	....
Log vol. " " "	....	....	....	....
Log wt. 1 c.c. water	....	....	......	....
∴ Wt. 1 c.c. water	....	....	....	....

Mean result of II and III = ...

Result by method IV* = ...

---

* Method IV is the one given in the laboratory work above.

LECTURE 4.

Let us now consider the results as obtained by the different methods we have employed.

The first noticeable feature is that the first method gives decidedly low results as compared with the others. Why is this? Is there any inherent reason why this method should tend to give results below the truth? We have already seen that there is some reason to distrust the method in that it assumes that the cylinder is a perfect one. A moment's reflection will show that lack of truth in the cylinder will as a rule tend to lower results; for since the circle encloses a greater area than any other figure of the same perimeter, it follows that any lack of truth in the bases of the cylinder will result in making the *real* volume as well as the *observed* weight of the displaced water less than it would be if the bases were true circles. Moreover, the *calculated volume* of the displaced water (which is the same as the volume of the *ideal* cylinder) must be above the truth. And since the weight of the displaced water is divided by the volume, it is clear that if the weight be *lowered* and the volume *increased*, the quotient must decrease. In other words, the result gained will be below the true one. Of course it is possible to imagine distortion of the cylinder which would result the opposite way (for instance, the "cylinder" might be barrel-shaped); but reflection will show that in the long run the most frequent distortion will be lack of truth in the bases; and the fact that the final and most careful determinations by this method invariably lead to results which are low in comparison with those obtained by other methods, confirms this view.

The results obtained by the second and third methods are higher; and the deviations from the mean are small and reasonably constant; showing the effect of increased precision in the method. The results obtained by the final method are of about the same character as those obtained by the third method, perhaps a trifle more steady.

Now how shall we combine these results so as to deduce from them the most probable value for the weight of one cubic centimeter of water at the temperature at which the determinations have been made. Shall we take a general average of the results obtained by all four methods? Certainly not; for our first series has been shown to contain a *constant error*: that is, the method has a tendency toward results which are below the truth. Clearly it is not of the same order of trustworthiness as the others. In an *average* or *mean* of several determinations it is essential that *all determinations* involved in that average be of equal "weight," or value, so far as can be determined by careful study. From this point of view the only safe course is to reject Series I entire.

Series II is free from this objection so far as can be seen, and with the refinement introduced by the use of the pipette it is, *so far as the volume measurement is concerned*, of about equal value with III and IV, which are, in this particular, alike. Between Series III and Series IV there is little choice. What difference there is is in favor of Series IV, but discussion of their relative merits would probably be an over-refinement. Series IV, however, represents probably the best and simplest possible manipulation with the instruments employed. Our final result, then, we will calculate from the results of the last three series.

LECTURE 5.

EVERYBODY knows what is meant when we say that one body is hotter than another. The statement implies that there is a certain difference in the condition of the two bodies; a difference which we can discern by mere contact with them, so that if we had several pieces of stone or iron, no two of which were equally hot, we should be able to arrange them in the order of their 'hotness' by the sense of touch alone.

Scientifically speaking, we say that a body which is hotter than another has a *higher temperature;* and in dealing with differences of temperature we recognize the fact that our sense of touch is neither delicate nor accurate enough to serve as a scientific means of measurement. We are accordingly obliged to make use of other means by which changes of temperature can be detected.

One of the indications of increase or decrease of temperature which is more commonly used than any other is the volume change which a liquid experiences as it grows hotter or colder, that is, as its temperature rises or falls. As a rule the volume rises as the temperature rises. Therefore, if we have a certain amount of liquid so arranged that we can readily observe any change of volume, we can tell whether an increase or decrease of temperature has taken place by noticing whether the volume has increased or decreased.

In putting this method into practice and undertaking to measure temperatures with accuracy, it is evidently necessary to have some standard; accordingly, we tell how hot a body is by stating how much its temperature is above or below a certain fixed temperature. The fixed point of temperature which has been selected as the standard, and is now, by common consent, employed everywhere, is the point at which ice and water are *in equilibrium;* that is, *the temperature at which, in a mixture of ice and water, the relative proportions of the two remain the same indefinitely.* It is not best, for reasons that will presently appear, to speak of it as "the freezing-point of water." It is more accurate to call it "the melting-point of ice," but the definition given above is better than either.

We are now in a position to consider how an instrument for measuring temperature can be practically constructed. In order to observe the volume change of the liquid it is put into a bulb provided with a long, slender stem of bore as uniform as possible, as in the case of the common mercury "thermometer."

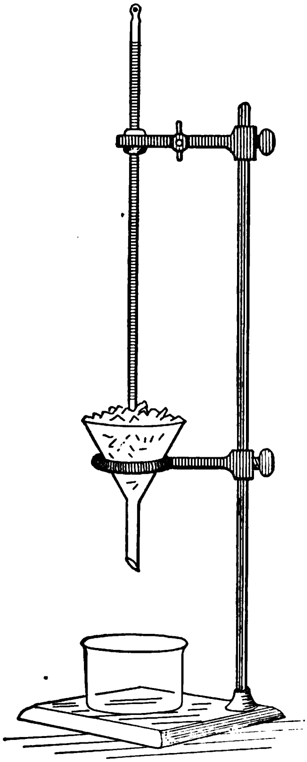
FIG. 8.

LABORATORY WORK.

The thermometers used for ordinary work in the laboratory are not made or graduated with any special care, and their indications are, as a rule, only trustworthy within a degree or two. It is therefore necessary to examine each thermometer before beginning to rely on its indications. First see if the 'zero-point' is correctly located. Fill a funnel with rather finely broken ice, and suspend the thermometer so that its bulb is surrounded closely by the ice. (See Fig. 8.) At the temperature of a comfortably heated laboratory the ice near the walls of the funnel slowly melts. In the interior, however, there is little or no melting, and the thermometer-bulb is surrounded by lumps of ice, each coated with a thin film of water; the thinness of this film insuring that the ice and water shall be at the same temperature. This is the closest approximation we can make to the conditions above specified, and with suitable care* they are realized perfectly.

The thermometer should be allowed to stand with its bulb thus packed in melting ice until the mercury column is stationary. It should then be recorded whether the zero-point on the thermometer-stem is correctly located or not. If it is incorrect, note and record by how many degrees, or by what fraction of a degree, it is in error.

There is a second fixed point on the stem, and that is the point marked 100°. It is supposed to represent the temperature of "free steam," i.e., steam that is escaping freely into the air, and whose pressure is, therefore, very closely atmospheric pressure. If the height of the mercury column in the barometer is 760 millimeters at the time the test is made, the mercury should stand exactly at 100°. If the barometer is high, the mercury will stand higher than 100°. If it is low, the mercury will stand lower than 100°. Every millimeter by which the barometer column varies from 760 millimeters changes the temperature of free steam by $\frac{1}{27}$ of a degree. This is for our purposes a very small correction; and if the barometer is only a few millimeters high or low, the difference is not worth noting.

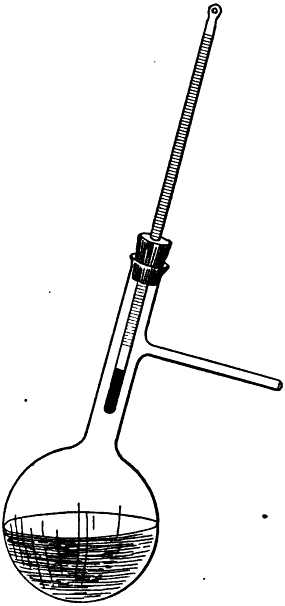
FIG. 9.

Arrange the apparatus for testing the correctness of the 100°

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* That is if there is plenty of ice, carefully packed, and if the melting at the outer walls is not very rapid.

mark as shown in Fig. 9,* noting as before and recording in your notes the amount, if any, by which it is in error. See that the water is kept boiling rapidly, and give the mercury column time to become constant before you take the reading.

Having thus tested the two principal fixed points, the next thing in order would be to examine the bore to see if it is uniform. For our present purposes, however, this is not necessary; since for some time all our readings will be either near 100° or near 0°, and the readings can be corrected if necessary by remembering to add or subtract the amount of the correction according as the error is minus or plus.†

The thermometer being properly corrected, prepare five solutions of common salt in water as follows:

Solution	I	5	grams	salt	in	100	cubic	centimeters	water
"	II	10	"	"	"	"	"	"	"
"	III	15	"	"	"	"	"	"	"
"	IV	20	"	"	"	"	"	"	"
"	V	25	"	"	"	"	"	"	"

[About 50 c.c. of each solution will be needed.]

Into the boiling flask, which should be of about 150 c.c. capacity, put first pure water. Mount the flask in position. Heat the water to boiling. Then make readings with the thermometer-bulb in the four following positions:

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* The boiling flask should rest upon a piece of wire netting supported upon one ring of a retort-stand. The neck of the flask should be held by a small clamp, or else steadied by passing it through the smallest ring on the retort-stand. See that the whole is neatly and symmetrically arranged. The hole in the cork of the boiling flask should be bored with a round file, and should be smooth and *in line*. It must be just small enough to hold the thermometer from slipping. The thermometer should be so placed that its bulb comes a little below the side tube. When the Bunsen lamp is put underneath to boil the water it should be turned on just enough so that the flame spreads out on the bottom of the flask in a spot about an inch in diameter.

† If it is desired to examine the bore more in detail, it can be done by detaching a thread of mercury (invert the thermometer and shake or tap it to accomplish this) and, moving this thread to different portions of the scale, noting the number of degrees it covers in each position. By this means it is possible to see where the bore is constricted and where it is enlarged.

1. Bulb of thermometer about ½ inch below the outlet-tube.

2. Bulb of thermometer about ½ inch above the surface of the liquid in the flask.

3. Thermometer-bulb just covered by the liquid.

4. Same as position 1.

Make exactly the same experiments with each of the five salt solutions.* Arrange the results in your note-book in the form of a neat table.

THERMOMETER-READINGS.

Solution Number	First Position.	Second Position.	Third Position.	Fourth Position.
I				
II				
III				
IV				
V				

Underneath this table make sketches of the thermometer in the four positions.

Write out a brief but clear review of your results as they stand, stating simply the facts as you have observed them.

What is the peculiar thing about the readings taken with the thermometer in the first position? Can you give any simple explanation? Catch a few drops of the liquid that condenses at the mouth of the side tube and evaporate to dryness in a porcelain evaporating-dish. Evaporate also about the same amount of the solution in the flask, and compare the results. Can you now explain your results as to the first reading? State, then, clearly and accurately any conclusions to which you are led by these results.

* The thermometer readings should be taken as promptly as possible.

What is the peculiarity of the readings taken in the second position? Does the quantity of salt in solution have anything to do with it? (Compare the result obtained with water.) What other possible causes are there? When you think you have found an adequate cause, devise an experiment to test the correctness of your view.

What can you say of the readings in the third position?

What is the peculiarity of the readings taken in the fourth position? Which set do they most resemble? What happens to the thermometer-bulb between positions 1 and 4? Do these considerations give any clue to the cause? Test your explanation by an experiment. To what conclusions do these fourth-reading results lead?

Having studied the boiling-points of these salt solutions, we may profitably investigate their freezing-points. For this purpose we require a few cubic centimeters of each of the solutions previously made.

First make a freezing mixture by filling a pint fruit-jar, or a vessel of similar size, with a mixture of ice and salt. A hole should be made in the center so that the test-tube may stand with its lower part surrounded by the ice and salt mixture.

The test-tube being in position, put in the first solution (about an inch depth in a test-tube) and stir the mixture gently with the thermometer. From time to time raise the test-tube slightly and examine the contents. The ice will separate in flaky crystals. When it begins to do so, remove the tube from the freezing mixture, stir, and read the thermometer. Wait till the ice *just begins to melt perceptibly*; then stir, and take another reading. If the quantity of ice be properly chosen, the two readings will agree.*

There should be about ⅛ as much ice as water (by bulk) in the test-tube when the readings are taken. Only the first three solutions need be frozen.

In carrying out these determinations watch closely and constantly the behavior of the mercury in the thermometer while the solution is in the freezing mixture. Keep track of it by making very frequent readings. When you have frozen one of your solutions, allow the ice to melt, then cool it down again, this time ***without stirring.*** Note and record the thermometer-readings every few seconds. This need not be done with more than one or two solutions.

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* That is with such thermometers as we are now using.

Finally make a determination of the "freezing-point" of water. The method is just the same, only the ice separates as a compact cylinder and not in the form of flakes.

Plot your results on cross-section paper.

LECTURE 6.

WHEN any liquid is being frozen, particularly when it is not stirred during the cooling, it will be observed that the temperature generally falls slowly until the separation of ice begins, and then *rises* rapidly to a point where it remains stationary. Which shall we take as the freezing-point?

We might call the point at which ice separates from the solution, or, in general, the point at which the solid separates out from the liquid, the freezing-point. But a serious objection to this designation would be that it is almost impossible to fix this point definitely, for the reason that the ice may separate at different temperatures according to circumstances.

For example, if a solution be allowed to stand quietly while it is cooling down, ice will, in general, separate at a lower temperature than if the solution be shaken or stirred. Another difficulty is that the temperature does not remain stationary when the separation of ice begins, but rises at once to another point where it does remain stationary; so that in order to get the first point we should have to take the reading very quickly, which would be a rather difficult matter.

If, however, we choose to take the point at which the mercury column finally remains stationary, we meet with none of the above difficulties.

In practice it is well to take two readings—one when a little ice has formed, and while the ice is still forming; the other when a little of the ice has melted, and while the melting is still going on. With such thermometers as we are now using the two readings should agree.

LABORATORY WORK.

Determine the effect of camphor, turpentine, or carbolic acid crystals upon the freezing-point of glacial acetic acid, using the same apparatus as in case of water. (Ice will do for the freezing mixture here.)

Determine in the same way the effect of camphor, turpentine, or naphthalene upon the freezing-point of benzol. (Ice and salt will be needed here.) Keep careful, systematic notes on your work.

LECTURE 7.

IT is a familiar fact that water left to itself, at ordinary temperatures, slowly evaporates. The same is true of practically all liquids. If this operation takes place in the open air, the whole of the liquid will ultimately evaporate; but if the liquid be allowed to stand in a closed bottle, the evaporation will not be complete unless the quantity of liquid be very small. This is a practical fact which is constantly utilized.

Now why is the evaporation incomplete in the confined space? Does the vaporization of the liquid cease? We cannot deny that the *decrease in amount of liquid* (evaporation), which is the visible sign that vaporization is taking place, ceases. After a certain amount of vapor has been formed, the amount of water is actually constant, as we can easily satisfy ourselves. Still, even this does not prove that vaporization has really ceased.

In attempting to find some satisfactory way of viewing the subject, it will be well to notice that there are other cases which are very much like the present one. For example, we have seen that when ice is stirred into water we reach after a while a point where no more ice melts. Similarly, when we dissolve such substances as salt or sugar in water we finally reach a point where the solution will take up no more of the solid.

Is it possible that in the evaporation of water in a closed vessel the space above the water becomes crowded to such an extent that no more vapor can find place? Let us submit the matter to experiment. Suppose that we have a bottle or flask so contrived that without actually opening it to the air we can introduce water drop by drop, as slowly as we please. Let us now, for the sake of convenience, surround the bottle with steam so that any small quantity of water will evaporate rather quickly. Let us now add a drop or two of water; wait till it evaporates, then add another drop, and so on till the last drop we add refuses to evaporate.

Next let us introduce a drop or two of some other liquid such as alcohol and see what takes place. We find that this new liquid evaporates readily and that subsequent drops continue to evaporate, but that after a while this liquid, too, refuses to evaporate into the space any longer.

If we continue the experiment we find that a third and a fourth liquid* behave similarly. Clearly, there is nothing here to suggest that the space is so crowded that no more vapor can form, and the following experiment makes it still less probable that such a state of things exists there.

If, as in the last experiment, we introduce water into the bottle slowly till evaporation ceases, and then raise the temperature, we find that we can vaporize a further quantity of water into the space, but that we finally reach a limit even at this higher temperature.

If we heat the bottle a little hotter, we find that we can vaporize still more water.

The most simple and satisfactory explanation of all these phenomena—which show themselves in connection with the melting of ice, the solution of salt, and the evaporation of water—is that they are cases of "equilibrium."

In the case just considered (the vaporization of water in a closed vessel), if we find that the apparent evaporation ceases after a while, then one of two things must be true: either the vaporization has stopped altogether, or *there is some process going on which restores water to the surface as fast as it evaporates.* We have seen that the first supposition is rendered improbable by several considerations. The second, on the other hand, is in perfect accord with all the facts hitherto brought out. Let us try to form in our minds some kind of a picture of this vaporization process. For example, we may think of the water as leaving the surface and passing into the confined space above the water as a *procession of water particles;* and this view is in accord with our experimental results. We have excellent evidence that when the water no longer diminishes in bulk the space over the water is not fully occupied, because we find that *under these conditions (without any increase of temperature) another liquid will evaporate readily into the same space.*

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* Ether, benzol, and chloroform are suitable liquids.

Still further, we have reason to believe, from our own observation, that these *particles* do not come to rest after they leave the surface of the liquid, but keep up their motion. For example, ether has a very decided odor. It is well known that if a little ether be poured out even in a room well protected from drafts, its odor will soon be perceptible in every part of the room.

Keeping now clearly in mind these two points, it is easy to see that when our particles have gained the space over the water and are wandering about in it, they must necessarily come in contact with its bounding surfaces. Now one of these bounding surfaces is *the surface of the liquid from which they originally came.* Striking this surface they may bound away again, or, if they strike forcibly enough, they may be entangled there, and thus become once more a part of the liquid. Clearly, this will happen the oftener the more particles there are in the space; and therefore as the space gets more and more crowded with particles, the restoration of the surface of the liquid will constantly become more rapid; and it is easy to see that there will ultimately come a time when the two operations of vaporization and surface restoration, or *condensation,* will be going on *at just the same rate.*

So long as this condition of things lasts there will be no gain or loss of liquid; that is, the *evaporation* will cease. The *vaporization*, however, goes on as before, and at just the same rate, so long as the temperature does not change.

LABORATORY WORK.

Measure out into 1½-inch flat crystallizing-dishes about 15 c.c. each of alcohol, chloroform, and water. Weigh each dish and record its weight. Place the dishes side by side on the table and allow them to stand there, weighing them at intervals of fifteen minutes or so. Which evaporates the fastest? Would the comparison be a fair one if the dishes were of different sizes? Compare in the same way the rates at which water and a strong salt solution evaporate. (Prepare and weigh them just before leaving the laboratory, and set them away until the next period, when they can be weighed again.)

Finally arrange a good tight fruit-jar (the "quick-sealing" jars are the best) as shown in the sketch (Fig. 10). In the bottom of the jar stands a crystallizing-dish containing concentrated sulphuric acid, calcic chloride, or some other material which absorbs water vapor readily. Put 5 c.c. water into a shallow crystallizing-dish or a deep watch-glass and support it over the other dish upon a little triangle made of glass rod or stout copper wire.

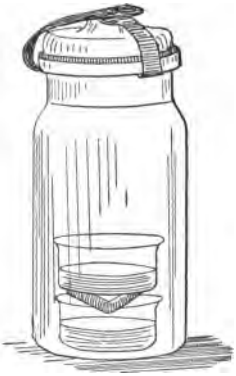

FIG. 10.

After putting the dish of water in position the jar is to be sealed and left to itself. Let some of the class try the same thing, only omitting the absorbing material. Compare the results.

LECTURE 8.

VAPOR PRESSURE, ITS MEASUREMENT, ETC.

We have seen that different liquids under the same conditions vaporize at different rates. Another way of expressing the fact that one liquid evaporates more rapidly than another is to say that it has a *higher vapor pressure*;[*] which means (if we continue, for the sake of convenience, to think of vaporization as the departure of a procession of particles from the liquid surface) that more particles leave its surface in a given time, and that the walls of the vessel in which it vaporizes are, therefore, subjected to greater pressure than in case of a liquid which evaporates more slowly. This is evident; for the pressure which a vapor exerts upon the walls of the confining vessel must be made up of the blows of the flying particles; and the more rapid the vaporization, the more pronounced will be the combined effect of the particles.

It is often of importance to be able to measure and compare vapor pressures. The principle of the following method will be easily understood, but it cannot be considered a good practical method.

First a *barometer-tube* is prepared. In its simplest form a barometer consists of a U-shaped tube like the sketch. If any liquid be poured into such a tube, it will stand at equal heights in the two limbs so long as there is the same pressure on the liquid surface in each. If, however, the pressures are different, the liquid in the two limbs will stand at different heights. In the ordinary barometer the tube is filled with mercury and there is no pressure at all upon the liquid surface in the long limb. The other limb is acted upon by atmospheric pressure, and the result is that the difference between the heights at which the mercury stands in the two limbs serves as a measure of the atmospheric pressure.

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[*] The term "vapor pressure" is, then, to be understood as meaning *the tendency of a liquid to pass into the state of vapor.*

If, now, we introduce a drop or two of some liquid into the long limb of the barometer and allow it to vaporize, its vapor will exert a pressure upon the mercury in that limb and the column of mercury will accordingly be depressed. The amount of such pressure can be recorded in terms of the number of millimeters by which the column is diminished in height. All vapor pressures are thus recorded.

It appears, therefore, that by means of such a barometer-tube we can measure, in millimeters of mercury, the vapor pressure of any solid or liquid at any temperature, since the top portion of the barometer-tube can be surrounded either with hot liquids or vapors, or by cooling mixtures, as we please. Nevertheless the method is, in actual practice, rather inconvenient; and the accurate measurement of vapor pressures presents a very difficult problem.*

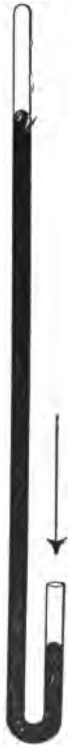

FIG. 11.

There is, however, a method which can occasionally be employed for studying the variation in the vapor pressure of a liquid with temperature or with other circumstances. It depends upon the principle that, other things being equal, the rate of evaporation varies with the vapor pressure; and it consists in comparing the weights of liquid evaporated from equal surfaces in equal times, but at different temperatures. We can also examine the effect of circumstances other than temperature (dissolved substances, for example) upon the vapor pressure of a liquid. To do this we have only to determine the weights evaporated from the liquid and from the solution in equal times, from equal surfaces, and at the same temperature.

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* See Ostwald's "Solutions," Chap. VII, particularly pp. 174–176.

LABORATORY WORK.

Compare the vapor pressure of water with that of salt solution No. 1 (see p. 18). Take two glass crystallizing-dishes of the same size (about 3 inches in diameter); clean them thoroughly, and put into one about half an inch of water, and into the other about the same amount of the solution. Take the temperature of the liquids in the dishes.* Place the dishes in the balance-pans and counterpoise accurately. Then set them on the desk, side by side; allow them to stand for half an hour or so; then place them in the balance-pans again and note which has lost the more weight. Take the temperature again. What temperature shall we take as the true temperature at which the determination has been made?

Compare in the same way the vapor pressures of water and another of the salt solutions and so on.

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* If the temperatures are not the same within a degree or so, let them stand on the desk *covered* for a few minutes until they are.

LECTURE 9.

BOILING. EFFECT OF DISSOLVED SUBSTANCES.

THE effect of heating water, or any other liquid, is to increase its vapor pressure. It is clear, then, that if we heat any liquid hot enough, its vapor pressure will finally rise to a point where it will be equal to the pressure of the atmosphere (indicated by the barometer at the time of the experiment). When this temperature is reached, a new condition is the result. At lower temperatures the vaporization takes place only at the surface of the liquid, and is, as we have seen, comparatively slow; but now that the vapor pressure of the liquid is equal to the atmospheric pressure, the formation of water vapor can take place at any point in the liquid; accordingly, we find that it takes place from those parts of the liquid which are the nearest to the source of heat, whatever it is.

Thus we notice that when water is heated in a beaker or any other dish, over a lamp, the temperature of the water slowly rises and the surface of the liquid remains quiet, until the thermometer indicates a temperature in the vicinity of 100°, when a new action begins. Bubbles of steam form at the bottom of the beaker, rise to the surface, and burst there; the steam goes off into the air, and the surface is thrown into more or less violent agitation by the ascent of the bubbles. This action is called *boiling*, and the temperature at which it takes place is called the *boiling-point*. It obviously follows, from what has just been said, that the actual boiling temperature as indicated by the thermometer will depend on the atmospheric pressure as indicated by the barometer. If the barometer indicates a pressure of 760 mm. of mercury, the boiling-point of water as indicated by a thermometer held in the escaping steam will be 100°.

If the barometer pressure is higher, the water will evidently have to be heated hotter before its vapor pressure becomes equal to the atmospheric pressure. If the barometer indicates a lower pressure than 760 mm., the vapor pressure will equal the atmospheric pressure before its temperature rises to 100°. That is, the boiling-point will be *raised* in the first case and *lowered* in the second.

It is clear, then, that whatever tends to lower the vapor pressure of a liquid will necessitate its being raised to a higher temperature before it boils. We have seen in our recent experiments that salt dissolved in water raises its boiling-point, and lowers its vapor pressure.

We have now seen the relation which vapor pressure bears to the *boiling-point*, as illustrated in our experiments with salt solutions of different strength. There remains the question of its relation to the *freezing-point*.

What is it that separates when a solution freezes? Is it the solid solvent (ice, in this case) or the dissolved substance, or both? Careful experiment answers that when a *dilute* solution freezes, what separates is, at first at least, *simply the solid solvent;* and it at once follows that the so-called "freezing-point" of a solution is simply the point at which *the solution and the solid solvent are in equilibrium, just as water and ice are at* 0°.

But why should dissolved substances cause a liquid to solidify at a lower temperature? Can it be that the lowering of vapor pressure has anything to do with the matter? The following diagram will enable us to study this subject.

On this diagram vapor pressures rise in proportion as we pass above the horizontal line, and temperatures fall (as indicated by the scale) as we pass to the right of the vertical line. Where the vertical line crosses the horizontal one the temperature is 0°.

First let us plot in a curve to represent the vapor pressure of water *below zero.* It may seem strange to think of working with water below zero, but by keeping the water perfectly quiet and taking care to have it free from dust its temperature can be readily carried several degrees below zero without its freezing. In fact we have already seen from our experiments that its temperature *usually* falls a degree or so below zero before it freezes. Moreover, its vapor pressure can be easily measured at these low temperatures by the barometer-tube method. By such means the vapor pressure of water below zero has been studied, and the curve is found to be of very much the form represented by the upper curve in the diagram. Now how about the vapor pressure of ice? Certainly ice has a vapor pressure, for pieces of ice will, in the course of time, disappear, even when the temperature is so low that no melting can take place. Moreover, this vapor pressure is easily measured by the

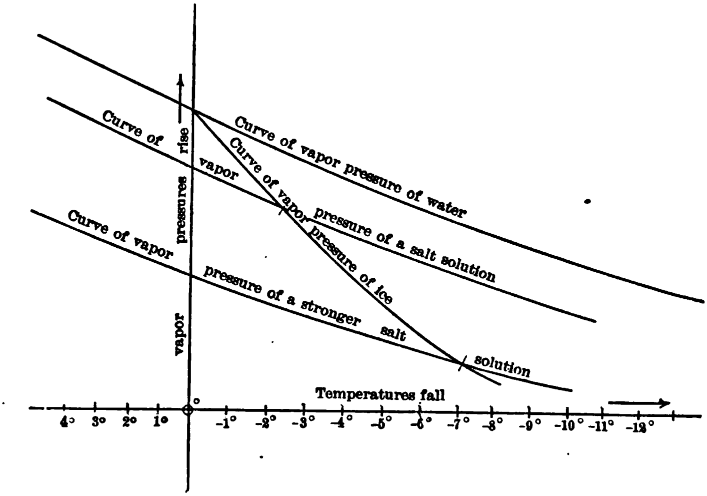

Fig. 12.

barometer-tube method, and we are thus enabled to draw the curve of ice-vapor pressure, of course below zero. We are not concerned here with its precise form; all we want is its general form. About that we know two things: first, that *at zero the vapor pressures of ice and water are the same.* This we know in two ways. In the first place all experience shows that at zero ice and water are in perfect equilibrium; that is, if given quantities of ice and water be mixed at 0°, there is no gain or loss on the part of either. If, however, we had ice and water in contact, and if the vapor pressure of ice, say, were greater than that of water, the vaporization of the ice would go on more rapidly than that of the water, and the relative proportions of the two would alter notably. In the second place, careful measurement shows that at 0° the vapor pressures of ice and water are the same. The same reasoning and similar experiments lead to the conclusion that *at the freezing-point of any dilute solution the vapor pressure of the solution is the same as that of the solid solvent.* Again, it is known from experiment that the vapor pressure of ice falls more rapidly, with falling temperature, than does that of water. Therefore if we draw a curve, as shown in the figure, we shall have one which will be, in its main features, correct.

It is easy to draw a line to represent the vapor-pressure curve of a solution. We have only to remember that the effect of dissolved substances is to lower vapor pressure, whatever the temperature; so if we draw a curve of the same general character as that representing vapor pressure of water, only *lower* at every point, we shall have one which will be correct enough for our purposes. Notice now where the ice curve crosses the solution curve, *for that is the temperature where the vapor pressure of ice and that of the solution are the same, and therefore where the freezing of the solution will take place.* You see that it is notably below zero; and you can see, moreover, that if we should draw in another curve (see dotted line) to represent the vapor-pressure curve of a still stronger solution, the freezing-point would be still more lowered. Hence we see that the lowering of the freezing-point and the raising of the boiling-point by dissolved salt are both due to the same immediate cause—namely, the lowering of the vapor pressure.

LABORATORY WORK.

Compare several substances with respect to their effects upon the boiling-point of water. Make in each case two solutions. One should contain 5 grams of the substance in 10 cubic centimeters of water; the other solution should be as strong as it can be made. For the substances use calcic chloride, potassic nitrate, cupric sulphate, magnesic sulphate, zinc sulphate, ammonic chloride. If convenient try the freezing-points of one or two of the solutions.

LECTURE 10.

In a recent experiment we saw that steam at a temperature of 100° could apparently heat a salt solution above 100°. We also saw that ice, having a temperature of 0°, could cool a salt solution below 0°.

These facts are of such great theoretical and practical importance that we must look at them a little more closely.

How can a body at 100° raise the temperature of another body in contact with it *above* 100°? There is certainly no mistake about the temperature of the steam, and we must accept the fact. If we do, it is clear that temperature must be a different thing from *that which raises temperature.* The following investigation will make this point still clearer. If we take a beaker containing a measured quantity of strong salt solution, say 100 c.c., and add to it 10 grams of water at 100°,* the rise in temperature is very slight indeed.

Let us take another 100 c.c. of the same salt solution, at the same temperature as in the previous experiment; but this time let us so arrange our wash-bottle that we can conduct *steam* into the beaker as it stands on the balance-pan. Notice the difference between the results of this and the previous experiment. The rise of temperature caused by adding 10 grams of steam is much more decided than in the former case. If we continue the addition of steam long enough, the solution finally *boils*, and the thermometer indicates a temperature above 100°. It is certain, then, that steam at 100° differs from water at 100° in having more temperature-raising power. Steam, however, is nothing but the vapor of water, and 100 grams of liquid water is the same thing in substance as 100 grams of steam; the only difference between them is that one is liquid and the other vapor. Hence it must be that it is in the act of passing from liquid to vapor that this temperature-raising power is acquired or stored up. We express this fact by saying that *heat* is absorbed, or stored up, and that a given weight of steam at any temperature *contains more heat* than the same weight of water at the same temperature. When we heat a beaker of water by means of a Bunsen lamp, the temperature rises until it reaches 100°. At that point, or a little above, the water begins to boil, and there is no further change of temperature: yet heat is being added by the lamp as fast as ever; and since the only other process which is going on is the change of water into steam, it is clear that the heat effects this change. So long as the steam remains steam, it contains this heat that it has absorbed in vaporizing; when it returns to water again, it gives it up. Strictly speaking, that which is stored up in the steam is not *heat*, but *energy*. It was the custom for a long time to speak of it as *latent heat*: and this is still done, for the sake of convenience. There is no harm in it so long as it is remembered that in the strict sense 'heat' means energy which reveals its presence through the thermometer.

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* This can easily be done by placing the beaker on a small pair of platform scales, counterbalancing, putting a 10-gram weight in the opposite pan, and adding the water from a wash-bottle in which the water is boiling. The jet of the bottle can be so placed as to point into the beaker, and the short outlet-tube being closed by a rubber tube and pinch-cock, the water will be forced through the jet into the beaker without stopping the boiling. When the 10 grams have been added, the short tube can be opened and the flow stopped.

The same general facts apply to the action of ice upon salt solutions. If we stir ice into a salt solution, the temperature falls *below* 0°, although the ice has a temperature of 0°. Here the fact is that it requires heat to change ice into water. The ice therefore abstracts heat from the salt solution into which it is stirred, and the temperature falls. The only limit to the temperature-fall is the freezing-point of the salt solution. If we make the experiment under such conditions that we have a saturated salt solution all the time, the limit will be the freezing-point of the saturated solution. This can easily be done in this way. We take some ice which has a layer of water on its surface, i.e., which is slowly melting, and stir salt into it. The result is that each lump of ice becomes coated with a little film of saturated salt solution. If now our ice be quite finely broken, so that there is a large surface of this strong salt solution in contact with ice, and if the mixture be protected from the warmer outside air by wrapping it with a towel or in some similar way, the temperature will sink to about – 21°, which is the freezing-point of a saturated solution of common salt. Such mixtures are called *freezing mixtures*. The most common one is that described above, which is cheap and convenient. Any salt, however, which when dissolved in water lowers the freezing-point may be used.

LABORATORY WORK.

Prepare several freezing mixtures, and test their temperatures. Calcic chloride and ice; potassic nitrate and ice; cupric sulphate and ice; ammonic chloride and ice, are good mixtures. The ice should be finely broken, and a small beakerful of each mixture prepared.

LECTURE 11.

We have thus far dealt with three forms of water: solid water, or ice; liquid water; and water vapor, or steam. So far as we know, these are the only forms in which water exists. At least there is no other form well enough defined to merit our attention at present. As we extend our studies to other substances, we find that they, too, always present themselves to our senses in one or more of these three forms, according to circumstances. For example, we ordinarily know iron in the "ice" or solid state; but at a sufficiently high temperature iron passes into a liquid, and at still higher temperatures can be vaporized. The same is true of silver, sulphur, copper, and many other substances which we ordinarily know only as solids.

Again, all the substances we ordinarily know as liquids can be "frozen" or solidified by cooling them sufficiently. Mercury, or "quicksilver," is a liquid at ordinary temperatures, but on cooling to about $-39°$ it freezes to a solid. Alcohol is a liquid, and it is only comparatively recently that it has been frozen, as its freezing-point is exceedingly low ($-130.5°$).

Finally, any of the substances we ordinarily know as vapors can be condensed to liquids, and afterwards frozen, though the temperatures often have to be very low to produce these results.

This may all be summed up as follows:

1. Any solid can be melted and afterward vaporized, provided it will stand the necessary heating without being destroyed. If we attempt to melt wood, we find that it ceases

to be wood, and is broken down into other things before its melting-point is reached; and the same is true of many other solids.

2. Any vapor can be condensed to a liquid; and the liquid thus produced can then be frozen, by reducing the temperature sufficiently.

The most characteristic feature of solids is their apparent inability to adapt themselves to any surface upon which they may be placed. They keep their shape, and can only be forced out of it by powerful pressure; when they either break, or slowly and reluctantly yield, something after the manner of pitch or asphalt. This latter mode of yielding is utilized in coining, wiredrawing, cold forging, etc.

Liquids differ markedly from solids in that they are capable of moving to any extent either downward or sidewise, but not upward. If we pour a little water into an irregularly shaped vessel, the water will settle down into every inequality of the vessel, but will not and cannot distribute itself upward at all. The result of this is that every liquid always has a *surface*, which in moderate-sized vessels is parallel to the surface of the earth. (We have seen that in small tubes the surface is bow-shaped. The same is true in large vessels, but the effect is not so noticeable as in small vessels.)

Vapors, on the other hand, distribute themselves in all directions; and have no boundaries except the walls of the vessel containing them. So long as there is space for them to fill, they will extend themselves so as to occupy it. A very little of any gas, illuminating-gas, for example, escaping into a room will in the course of time make itself perceptible in every part of the room by its odor.

We may now compare these three forms of matter with respect to another property.

Solids, liquids, and vapors follow the same general law as to their behavior when their temperature changes. They all undergo change of volume, and as a rule they increase in volume (expand) when heated, and decrease (contract) when cooled.

They differ, however, in the extent to which they change their volume for a given change of temperature. Solids show the least change, liquids more, and vapors the most.

We are not particularly interested in these facts with relation to solids and liquids. Every solid and every liquid has its own particular rate of expansion. In the case of vapors, however, there is a very remarkable fact which is of the greatest interest to us. When vapors exist out of contact with their liquids, and at temperatures far above their condensing-points, they all show *the same rate of expansion* no matter what the vapor may be.

For example, air must be regarded as the vapor of a liquid with a very low boiling-point. It has actually been condensed to a liquid and frozen; but its condensing-point is enormously low, and therefore liquid air has no permanent existence at ordinary temperatures and pressures. Therefore air is a vapor in the condition mentioned above; and there are a number of other substances which are known at ordinary temperatures and pressures only in this condition. We call them *gases*, and we shall use this term hereafter. Fig. 13 will serve roughly to picture the relative behavior of solids, liquids, and gases with changing temperatures.

The diagram brings out the fact that liquids change more for a given temperature-change than do solids, and that gases change more than do liquids.

It does not tell the whole truth, however, as we shall soon see. In the first place, as the temperature of a solid approaches the melting-point, the solid always begins to show irregularities of expansion. As a rule, the expansion rate increases, and the substance begins to expand more like a liquid. A similar change takes place in all its properties. It is in a sort of transition state. The same is true of a liquid when its temperature is brought near either its boiling- or freezing-point. In the first case its expansion rate rises rapidly, and approaches that of the gas into which it is presently to change; in the latter case its expansion rate falls and becomes more like that of the solid. The result is that it is usually only within rather narrow limits of temperature that the expansion rate of a solid or a liquid is constant, but after a substance has once become a gas its expansion rate *is* constant. That is, no matter how high the temperature may be carried, the increase will be the same for a temperature-change of one degree in one part of the scale as in another. This matter will be considered in more detail in the next lecture.

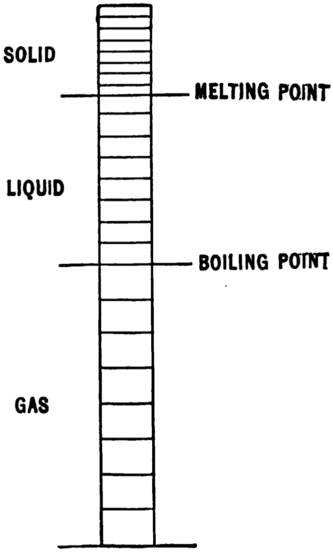

Fig. 13.

Strangely enough, although solids appear to be the most tangible form in which substances present themselves to us, the science of chemistry has been built up largely upon facts derived from a study of gases, the least tangible, at first sight, of the three forms. It will therefore be advisable for us to enter the field by this path; and it is possible to select two gases, a study of which will lead us into the subject more rapidly than would be practicable in any other way.

We will begin our study, then, by determining the weight of a given volume of one of these two gases.

The method followed will be to heat in a suitable vessel a weighed amount of a certain mixture which yields, upon heating, the gas we desire. The weight of gas given off we shall determine by the loss in weight of our materials. The volume of gas given off we shall determine by collecting and measuring it.

LABORATORY WORK.

Set up the apparatus shown in the figure (Fig. 14). *A* is a piece of hard combustion-tubing sealed at one end, about 15 cm. long, and 1.5 cm. internal diameter. This tube may be grasped by a clamp near the cork, and fixed to a ring-stand, or it may simply rest upon one of the rings of a ring-stand or upon a tripod. It should incline backward about as represented in the sketch. Select a smooth sound cork, and bore a *smooth* hole through it with a round file. Next prepare the small bent tubes shown in the figure. See that all bends are symmetrical, and in the same plane.

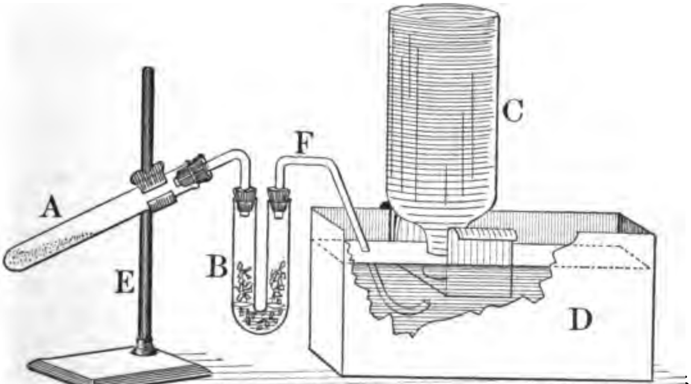

FIG. 14.

B is a small U tube. It should be filled about as shown with glass beads, small fragments of pumice-stone, broken glass, brick, or tiling, whichever is most easily available. In any case the fragments should be about the size of a small pea. Finally pour in enough strong sulphuric acid *just to close* the bend, as shown in the sketch.‡ The stoppers for this tube are single-bored rubber ones. When the apparatus is put together it should be perfectly tight, compact, and neat. All tubes should fit *tightly* in place. Each piece of apparatus should be *critically* inspected by the teacher before the student is allowed to proceed.

C is a "lithia bottle" or any bottle capable of holding about two litres. It is filled with water, and inverted so that its mouth is under water and rests upon the shelf of a "pneumatic trough."

Everything being ready, weigh roughly about 6 grams potassic chlorate and 4 grams manganese dioxide. Mix them in a small mortar or on a sheet of smooth paper. Wipe tube *A* inside and out with a dry, clean cloth, and put in the mixture. Incline the tube, and tap it until the mixture spreads out as shown in the sketch. Remove the delivery-tube *F*, and carefully counterpoise the part of the apparatus consisting of tubes *A* and *B* with their connections. (Use no weights; but fragments of brick, pebbles or shot, and finally sand.) Remount the apparatus in position as shown, and begin heating tube *A* with a *low* Bunsen flame; heating first at *E* and working gradually back. Watch the rate at which gas comes off, and regulate the heating so that it does not become too rapid. When no more gas is given off, *at once* remove the delivery-tube *F*; then allow the apparatus to cool. When it feels cool to the touch, remove all stoppers for a few minutes, so that the whole apparatus may be filled with air as it was at the previous weighing. Finally replace the stoppers; hang the apparatus on the balance again, and add weights until the whole is in perfect equilibrium. The weights added give the weight of gas evolved.* Record it at once.

Take the temperature of the water in the pneumatic trough. This temperature may be regarded as the temperature of the gas in the bottle provided it has not stood too long. Record this temperature and the barometric pressure, as they will both be needed in the final calculations.† Next cover the mouth of the bottle with a piece of smooth paper; remove the bottle from the trough, and set it upright upon the desk. It will contain a little water and the gas. In order to find the number of cubic centimeters of gas present in the bottle we have only to fill up the space at present occupied by gas with water from a graduated cylinder, noting carefully the number of cubic centimeters added.

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* When the experiment is finished drain the acid from the U tube and set it aside with the beads still in it.

† This can be done while the tube and its contents are cooling.

‡ Calcic chloride does as well.

We have now determined (1) the weight of gas evolved; (2) the volume of gas evolved; (3) the temperature and pressure at which the gas was collected. The calculations will be explained in the next lecture.

LECTURE 12.

LET us suppose that we have, confined in a glass tube at a temperature of 0°, a certain volume—say one cubic centimeter—of air or any other gas. Let the air be included between the bottom of the tube which is sealed, and the little plug of mercury *C* which is also to serve as an index (see Fig. 15). We have now practically a thermometer in which we use air instead of mercury, and we can watch the increase or decrease of volume by noting the movements of the mercury index. If, now, we immerse the bulb of our thermometer, i.e., the space *CD*, in broken ice, we have one cubic centimeter of air at 0°.

Now let us raise the temperature by 1°.* The mercury index moves upward, and the volume increases by a certain small amount which can be measured. This small fraction will always be found to be $\frac{1}{273}$ of the original volume. That is, the volume of the gas at 1° is $1 + \frac{1}{273}$ c.c. If we carry the temperature up another degree, we find that the mercury moves again and the volume increases by another small amount, which is the same as before. That is, the mercury moves the same distance while the temperature passes from 0° to 1° that it does while the temperature passes from 1° to 2°. The increase in volume is, as before, $\frac{1}{273}$ of the original volume, and hence the volume at 2° is $1 + \frac{2}{273}$ c.c. To make a long story short, the same thing will appear no matter how far the temperature is allowed to rise; and hence, if we carry the temperature up to 273°, we shall have for the volume of our gas $1 + \frac{273}{273}$ or 2 c.c., that is, the volume is just double what it was at 0°.

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* Throughout this discussion of temperature effects pressure is supposed to remain constant.

Let us start again at 0° with our 1 c.c. of gas, and this time lower the temperature degree by degree instead of raising it. On lowering the temperature to $-1°$, we find that the mercury moves downward, and the volume therefore shrinks; but it shrinks by the same small fraction as it formerly increased, namely $\frac{1}{273}$, and our volume at $-1°$ is $1 - \frac{1}{273}$ c.c. For $-2°$ it is $1 - \frac{2}{273}$, and so on; until, if we should carry the temperature down to $-273°$, the volume would be apparently $1 - \frac{273}{273}$ or 0 c.c. We say "apparently," since it is obvious that the experiment is impracticable. In the first place, we have not yet been able to reach such a low temperature. The lowest temperatures hitherto obtained are in the vicinity of $-240°$. At this temperature practically all known gases have become liquids, and most of them liquefy long before this temperature is reached. Moreover, we have seen that as a gas approaches its condensing-point it begins to partake of the nature of the liquid into which it will presently change, and consequently the regular rate of expansion that prevailed at higher temperatures no longer holds. It is therefore idle to speculate on the interpretation of what we found would be true if gases continued their regular contraction rate downward indefinitely. The only interest the matter has for us is that it enables us to devise a purely arbitrary scale of temperatures which is very convenient when we are dealing with gases. This scale of temperatures has its zero-point located at $-273°$ on the ordinary thermometer-scale; and the advantage of it lies in the fact that on this scale the volumes which a gas occupies at two different temperatures are *proportional to the temperatures* on this new scale; so that if we know the volume occupied by a gas at a certain temperature, we can immedi-

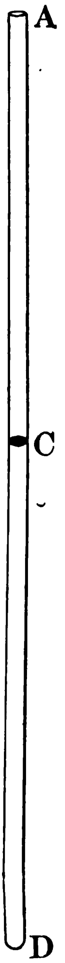

FIG. 15.

ately calculate what volume it will occupy at any other temperature.

For example, suppose we have measured 1200 c.c. of air at 10°, and ask ourselves what the volume will be at 23°. First of all we must convert our temperatures into temperatures on our new scale, or *absolute* temperatures. This is easy, since 0° on our ordinary scale corresponds to 273° on the new scale. Thus:

Ordinary.		Absolute.
0°	=	273°
−1°	=	272°
−3°	=	270°
	etc.	
−273°	=	0°

Ordinary.		Absolute.
0°	=	273°
1°	=	274°
3°	=	276°
etc.		

Therefore any temperature on the ordinary scale, whether above or below zero, can be converted into the corresponding temperature on the new scale by adding 273° to it.

In this case our temperatures are 10° and 23°, which become, by adding 273° to each, 283° and 296°.

Now since the volumes are proportional to the temperatures on the new scale, we have

$$1200 : 283 :: x : 296,$$

or $$x = 1200 \times \tfrac{296}{283} = 1255.+ \text{ c.c.}$$

When once the principle of the above calculation is grasped, it is simpler and quicker to notice, in such a problem, in which direction the change is to be; i.e., whether the volume will increase or diminish. If it increases, multiply the original volume by the higher temperature and divide by the lower. If it decreases, multiply by the lower temperature and divide by the higher.

Since gases behave in this regular manner with reference to their expansion rates, it is not surprising to find that they show the same regularity in their behavior when compressed.

The result of all measurements has been to show that gases change their volume with change of pressure, and that the greater the pressure the less the volume.. In other words, ***the volume occupied by any gas is inversely as the pressure***, the temperature being constant.

If we take 1000 c.c. of air at a certain measured pressure, and double this pressure, the volume of the gas will be halved. If we halve the pressure, the volume doubles; etc.

Now keeping the above facts in mind it will be seen that if we know the volume occupied by a gas at a given pressure, we can calculate what volume it will occupy at any other pressure. Suppose we have 1200 c.c. of gas confined at a pressure of 730 mm. What will the volume become at 760 mm.? Since the volumes are inversely as the pressures,

$$1200 : 760 :: x : 730.$$

$$x = \frac{1200 \times 730}{760} = 1156.+ \text{ c.c.}$$

Finally, we can, if we wish, apply both corrections at once. Suppose we have 1200 c.c. of a certain gas measured at 10° and 760 mm. What will be the volume at 23° and 740 mm.?

First we convert our temperatures into absolute temperatures by adding 273° to each, and they become 283° and 296°. Then correcting for temperature we nave $1200 \times \frac{296}{283}$; and correcting further for pressure, noticing that the new pressure is lower than the old one and so will increase the volume, we have $1200 \times \frac{296}{283} \times \frac{760}{740}$.

A convenient form in which to put the work is as follows:

$$\begin{array}{lr@{\qquad}lr}
\text{Log } 1200 = & 3.07918 & & \\
\text{“} \quad 296 = & 2.47129 & \text{Log } 283 = & 2.45178 \\
\text{“} \quad 760 = & 2.88081 & \text{“} \quad 740 = & 2.86923 \\
\hline
& 8.43128 & & 5.32101 \\
& 5.32101 & & \\
\cline{2-2}
& 3.11027 = 1289.+ \text{ c.c.} & &
\end{array}$$

From what we have seen of the laws of gases thus far, it will easily be understood that the *density* of any gas (that is, the weight of one cubic centimeter of it) will change with every change of temperature and pressure; and that if we wish to compare gases as to their density, we must compare them at the same pressure and temperature. It is customary, therefore, to give the densities of gases at a certain selected temperature and pressure; the selected temperature being 0° and the pressure 760 mm., which is the normal height of the barometer column at the sea-level. Therefore, in the determination of the weight of 1000 c.c. of the gas we have been working with, we must, before making our final calculation, correct the volume of gas collected to what it would be at 0° and 760 mm. Since we have noted the temperature and pressure of the confined gas, this is an easy matter, and the calculation is made just as above. There is one other correction to be applied in this case, however. The gas has been collected *over water*, and the space over the water contains *water vapor*, which, as we have seen, exerts a certain pressure depending upon the temperature; therefore the pressure inside the bottle (when the water-levels inside and out are the same) is the pressure of the gas + water-vapor pressure, while outside it is simply atmospheric pressure. *But what we want is simply the pressure exerted by the gas we have collected.* We cannot easily remove the water vapor, but we can do what amounts to the same thing: we can subtract the *pressure of the water vapor*, expressed in millimeters of mercury, from the barometer pressure, and the result will give us the *corrected barometer pressure*, and this we use in our calculation.

LECTURE 13.

THE next problem we have before us is to determine the weight of 1000 c.c. of a second gas. We shall follow the same general method as before; that is, we shall evolve the gas from carefully weighed or counterpoised materials, determining the weight of gas evolved by the loss of weight of the apparatus and materials. We shall collect the gas evolved over water, measure its volume, and, after making the necessary corrections, deduce our result.

The present problem presents, however, much greater difficulties than the preceding one, and nothing but the utmost skill and intelligence we can bestow upon it will enable us to obtain results of any steadiness or value. In the first place, the gas is very much lighter than the previous one, and shows a correspondingly greater tendency to leak out of the apparatus if all the joints are not perfectly tight. Now our intention is that all the gas evolved shall find its way into the bottle in which we collect it, and that none of it shall go anywhere else; hence the greatest care must be taken that all opportunities for leakage are reduced to a minimum.

LABORATORY WORK.*

Fig. 16 shows the apparatus employed. The small flask has a capacity of about 100 c.c. All the stoppers are rubber ones with smooth surfaces.

The first U tube contains glass beads and enough of a strong solution of potassic permanganate acidified with dilute sulphuric acid to fill the bend. Its use is to arrest small quantities of other gases which are formed during the process, and which would otherwise leave the apparatus. The second U tube is

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* Recent experience has shown (1) that a single U tube carefully filled with granulated calcic chloride is sufficient, and (2) that the acid in the flask should be of such strength that all the gas is evolved within ten minutes.

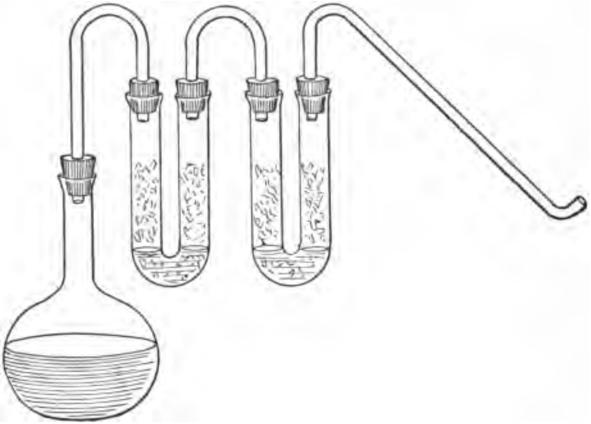

FIG. 16.

fitted up exactly as in the previous experiment. The joining pieces should be carefully and neatly bent and the whole thing should be *as compact as possible.* Whenever a glass tube is passed through a rubber stopper, it must come *entirely through* and protrude a little on the other side. Each stopper should have at least ¼ inch bearing on the glass. The stoppers may be made tighter by rubbing into them *thoroughly* a little vaseline, after which the stopper should be carefully freed from all adhering vaseline. It takes only the least film to produce the desired effect. When all is ready, the flask should be about ⅜ filled with dilute sulphuric acid, and the entire apparatus, after being thoroughly wiped with a clean, dry cloth, should be set on the desk and allowed to remain there for five or ten minutes.

Meanwhile some strip zinc should be cut into pieces which will easily go down the neck of the flask. Clean them with a file or a piece of sandpaper: then weigh out about 5.5 grams of the cleaned zinc, recording the exact weight taken. When this has been done, hang the apparatus by means of a little loop of copper wire from one of the suspension hooks of the balance; place the zinc in the same pan, and counterpoise the whole *with* *the utmost possible care.* In counterpoising the apparatus be sure that sufficient time is given for the equilibrium to become constant. It may happen that it takes about all the period to fit up the apparatus and fill the U tubes. If so, let it be hung on the balance the last thing before leaving the laboratory and left overnight. Once established the equilibrium is surprisingly constant.

After the counterpoising has been attended to, the delivery-tube should be attached, and the apparatus set up close to the pneumatic trough. The lithia bottle in which the gas is to be collected being in place, remove the stopper from the flask, quickly put in the zinc, and adjust the stopper to its place again as tightly as practicable.

Evolution of gas will soon begin, and will increase in rapidity without any heating. Indeed, it is a good plan to set the flask in a dish of cold water to prevent heating, since the mixture grows warm of itself during the evolution of the gas, and it is desirable to have as little water as possible vaporized from the flask.

When all action has ceased, the delivery-tube is to be detached and thoroughly cooled. It is then to be opened (U tubes and all), so that the gas inside may be replaced by air; thus bringing the apparatus into the same state in which it was previously counterpoised. This will take about two minutes. The apparatus is then put together, thoroughly wiped as before, hung on the balance, and the lost weight determined by adding weights from the box. The same precautions are necessary as at the other counterpoising.

Meanwhile the volume of gas collected can be measured, the thermometer and barometer observed, and the necessary corrections to 0° and 760 mm. made as in the previous experiment. Finally, when the loss in weight—that is, the weight of the evolved gas—has been ascertained with all possible care, the weight of 1000 c.c. of the gas at 0° and 760 mm. can be calculated.

It will be seen that in this experiment our final calculation consists in dividing the weight of gas collected by its volume. The volume will be something like 2000 c.c., and the weight will probably be from 0.15 to 0.18 grams. A moment's reflection will show which of these quantities must be determined with greater precision. A variation of a few cubic centimeters in the volume will make very little difference in the result as calculated; but an error of a single centigram in the very small dividend, i.e. the weight, will make a great difference.

Satisfy yourself on this point by a few trial calculations. Compare, also, this and the preceding experiment. It will then be easily seen why this last experiment is so much the more difficult; namely, because the weight, i.e. the dividend, is necessarily so much smaller with reference to the divisor.

How many decimal places shall we retain in the final result?

LECTURE 14.

THE results of the last two experiments will be better appreciated after a review of the properties of gaseous substances.

We have seen how remarkable is the regularity in the behavior of gases under change of temperature and pressure. It will be remembered that they all behave alike. Now this fact of itself certainly seems to point to some corresponding regularity in the internal structure of gases; and we may well raise the question, in what does this regularity consist? The answer to this question takes us back to the fundamental ideas held by chemists as to the inner structure of what we call matter, whether solid, liquid, or gaseous.

In our studies on vaporization, as will be remembered, we found that we could best understand the matter by regarding the process of vaporization as the passage of a procession of water-particles from the liquid surface into the space above. It was also seen that we had reason to believe that after these particles left the surface they still remained in motion, and wandered about in the space above the water.

When a cubic centimeter of water at 100° changes into steam at 100°, it occupies about 1700 times the space it formerly occupied as water. So that, if we hold to this idea of particles, it would seem as if liquid water and steam differed in this, that in the steam the water-particles are on the average farther apart than in liquid water. Moreover, we have good reasons for believing that solids, though much less easily distorted than liquids and gases by application of any force to them, are really not absolutely solid; but that they, like liquids and gases, are composed of particles in motion, but having a very restricted field of motion. So simple is this idea, and so satisfactorily does it explain the facts with which we are acquainted, that it seems at present, and has seemed for many years, the most rational and sensible view to adopt as a fundamental one.

On this basis we think of steam as a collection of an immense number of *water-particles*, each one of which is exactly like every other one. These little particles we think of as separated from each other by distances which are comparatively great, when we consider the size of the particles themselves; and, finally, we think of them as in rapid motion. It will be our business, as students of chemistry, to study these same particles more in detail, and to gain more definite ideas concerning them; but the conception as above stated is sufficiently definite for our present purposes. It will be seen that we are leaving solids and liquids out of consideration for the present. We know very little about them. Such facts as are important for our purposes will be considered later. Just now it is important to see how this "particle" idea helps us to understand the regular behavior of gases under changing temperature and pressure.

If we regard a gas as a collection of rapidly vibrating particles, it is clear that similarity in the behavior of any two gases must be due to a corresponding similarity either in the *nature* of their particles or in the *number* of particles contained in a given volume at the same temperature and pressure. Following out this line of thinking, Ampère, in 1814, adopted the simpler of these two alternatives, and proposed to explain the facts now under consideration by the hypothesis that *in equal volumes of any two gases at the same temperature and under the same pressure there are the same number of particles.*

The same idea had been suggested by Avogadro in 1811; but he reasoned from another set of facts altogether. We shall find the history of this idea an interesting one later.

For the present all that need be said is that this view is in perfect accord with all known facts, and explains in a clear, sensible manner not only the facts we are now considering, but hosts of others.

Its main interest for us just at present is that it enables us to attach a new significance to the results we have obtained in the last two experiments. If equal volumes of any two gases contain the same number of particles when measured at the same temperature and pressure, then our results mean that the particle of the first gas is about 16 times as heavy as the particle of the second gas; for if there are the same number of particles in one liter of the first gas as in one liter of the second, both being at 0° and 760 mm., then it is clear that the only difference between the weights of these equal volumes must be in the weights of the individual particles.

If, therefore, we should make similar experiments upon all other known gases, our results would enable us to compare the weights of the representative particles of these gases; and if there should happen to be some gas whose particle was lighter than any of the others (as of course there would be), we could, if we chose, take this lightest particle as a standard, and compare all other particle weights with it, in the same way that we commonly compare the weights of different bodies with our brass gram weight, and record their weights in grams and fractions of a gram. Moreover, this can be done in case of substances which are not gases at the ordinary temperature, provided we can, by application of heat, convert them into gases at a manageable temperature. For example, water is not a gas at ordinary temperatures; but at 100° it assumes the state of a vapor, and at a temperature of about 130° or 150° behaves like any gas; or, at least, nearly enough for our purposes. Alcohol boils at 78°, and its vapor at 100°, or so, is far enough above the boiling-point to be treated as a gas. Other liquids can be similarly treated. In any case, all that is necessary is to seal up a flaskful of the vapor at a sufficiently high temperature, this temperature being carefully observed and recorded, as well as the atmospheric pressure as indicated by the barometer. Since care is always taken that when the flask is sealed the gas shall be at atmospheric pressure, the barometer-reading gives us the pressure under which the gas is confined. We can now cool and weigh the flaskful of vapor; and then by opening and carefully cleaning the flask, exhausting the air by means of an air-pump, and weighing again, obtain the weight of the flask alone. The difference between these two weights is, of course, the weight of the vapor at the observed temperature and pressure. All that remains is to compare this weight with the weight of the same volume of that gas whose particle is taken as the standard. Of course this only gives a rough outline of the method. In order to secure results of any value it needs to be very carefully carried out. Nor is it the only method. There are several others. This one is described because it is rather the simplest in principle.

While the idea of comparing the weights of particles is a striking and interesting one in and of itself, it gains a new significance and a new interest in the light of a line of facts to which we now turn our attention.

LABORATORY WORK.

For the following experiments, in which you are to work primarily with the lighter of the two gases now under study, it will be necessary to have at hand some form of *generator*, by means of which a supply of this gas can be obtained.

A very convenient and satisfactory form is shown in Fig. 17. It consists of a 250-cc. flask fitted with a double-bored stopper, through one hole of which passes a straight glass tube open at both ends. To the lower end is attached, by one or two rubber bands, a bundle of zinc strips each about ½ an inch wide and 2 inches long. The bundle of strips is attached in such a way that when the end of the glass tube is ¼ of an inch under the surface of the liquid in the flask the bundle of strips does not touch the liquid. The flask is ⅔ filled with dilute sulphuric acid.

A drying-tube is connected as shown in the sketch. In this case the two limbs of the U tube should be well filled with glass beads moistened with strong sulphuric acid, *but there should not be acid enough to seal the bend,* since in this case we could not get a perfectly steady current of gas as will be necessary in some of our experiments.*

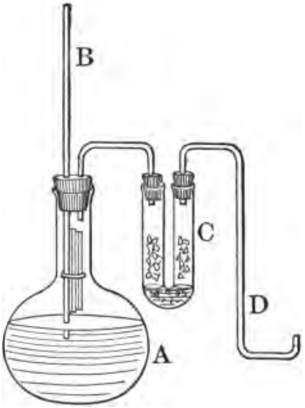

FIG. 17.

Since in a portion of the work the hydrogen is to be lighted at the orifice from which it issues, the following additional arrangement will be found very serviceable: Take about an inch from the small end of the stem of a clay tobacco-pipe, and adapt it, by means of a short length of rubber tube, to the end of the delivery-tube. The hole in the pipe-stem may be too large, and the best way to fix it is to plug the small end with a little fine clay or plaster of Paris, and then carefully bore out a new hole with a pin. Finally heat the jet thus prepared in the flame for a few minutes to harden the clay. This little arrangement permits of maintaining a flame as long as may be desirable without the danger of the orifice becoming sealed, as it so often does when a glass jet is used.

Everything being carefully and neatly set up, the generator should be charged with dilute sulphuric acid (about 1 : 5½); it should then be placed so that the end of the delivery-tube is under the water in the pneumatic trough, and within about half an inch of the surface, *the pipe-clay jet being, for the present, disconnected.*

The straight tube carrying the bunch of zinc strips is now pushed down through the stopper until the zinc is partially immersed. Evolution of gas will soon begin, and the first step is to make sure that all air has been swept out of the flask. To this end collect some of the gas over water in a test-tube. When the test-tube is full, remove it from the trough, and bring it *mouth downward* near the Bunsen flame. Continue to make tests in this way until the gas simply takes fire at the mouth of the test-tube and burns *quietly*.

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* Although the drying-tube is not essential for some parts of the work, it will be as well to have it attached all the time. Calcic chloride may be used as a dryer if more convenient.

The student should now answer for himself the following questions:

1. Has the gas any color?

2. Has it any odor? (Compare the odor of the gas prepared as above with that of the same gas after it has been passed through an acid solution of potassic permanganate, as in the last experiment.)

3. Is it heavier or lighter than the air?

4. What happens when a lighted match is pushed up into an inverted jar full of the gas? (A small wide-mouthed bottle is serviceable here. The match should be attached to a piece of copper wire, or else stuck into the end of a short piece of small glass tubing.) Try also a little fragment of glowing charcoal held in a loop of wire. Record simply what you see and are sure of—nothing else.

5. Is it perceptibly soluble in water? Of course it is clear, from the fact that we collect it over water, that it is not very soluble, but it does not necessarily follow that it is not soluble at all.

A dry test-tube should be filled with the gas (How?), closed by the thumb, and inverted with its mouth under water. The tube should then be inclined until a few bubbles of gas escape, their place being taken by water. Lower the tube till the water-levels inside and out are the same; mark the level by a piece of thread or a small rubber band; then close the tube with the thumb once more, and shake gently so as to bring the gas thoroughly in contact with water. Bring the mouth of the tube under water again, and remove the thumb. How does this method show whether a gas is dissolved by water or not? (It will be a good plan to try this with some gas that dissolves quite readily in water, in order to see how the result appears.)

Next dry out the delivery-tube of the generator by a strip of filter-paper (without detaching the tube from the generator).

Attach the pipe-clay jet; then light the gas as it escapes at the jet.

1. Note carefully the form and color of the flame.

2. Lower a clean dry fruit-jar or a flask over the flame mouth downward. Watch carefully what happens. Dry the jar again, and this time lower it at once until the mouth of the jar is sealed by the water in the pneumatic trough. Record carefully your observations. Repeat the experiments several times.

Can you detect any of the unburned gas beyond the flame? How do you propose to experiment on this point?

LECTURE 15.

THE fact to which we now turn our attention is one which has been observed by you in your laboratory work; namely, that the lighter of the two gases we are studying *burns* in the air. It is a fact which, if we carefully study it, will lead us to some interesting conclusions. The first thing to do is to get the conditions clearly in mind. The gas comes along through this tube, and at the exit there appears, when a match or any burning body is brought near, this peculiarly shaped thing which we call a *flame,* and with which we all associate certain ideas. For example, it always appeals to the eye, more or less. This one is not particularly luminous; but is, nevertheless, visible. Again, we always think of a flame as hot, and this one is no exception. Still further, a flame like this, which is kept going by a steady supply of gas from the generator, has a peculiar and characteristic shape. If the current of gas be increased, the flame, as you see, increases in size; but its shape remains about the same. If the current be decreased, the flame grows smaller, but still maintains its shape.

Now let us turn our attention to some features which are not quite so obvious. The first of these we can best see by holding a dry jar down over the flame as it burns. You see the jar is immediately dewed over with moisture; this was noticed in your laboratory work. Now when we see a dew-like film form on a dry surface in this manner, we always ascribe it to the condensation of some liquid on the surface; and so here we seem to be dealing with a liquid which has condensed, from the state of vapor, on the glass. We may well inquire, Whence comes this liquid; and why does it appear in the neighborhood of the flame? Does it appear in the neighborhood of *any* flame?

Let us try the experiment with the following representative substances: sulphur, phosphorus, a candle, and a piece of magnesium ribbon. We see that in some of these cases a liquid appears, in others not; but there always appears *something*. For instance, in the case of the sulphur you see no liquid form, but there is formed a gas with a choking odor. With phosphorus, and with magnesium, we get white, snow-like solids; while in the case of the illuminating-gas and the candle liquids appear. We might go on much farther; but we have already gone far enough to find flames which are accompanied by the appearance of liquids, solids, and gases. Moreover, since all these substances were burned in the air, it seems probable that the nature of what appears during the burning depends, partly at least, on the nature of the substance burned.

In order that we may form some idea of the real importance of what we have seen, it will be well to conduct an experiment in such a way that we can burn the flame for a considerable length of time and collect the product which appears. For this purpose a piece of combustion-tubing about 14″ long is clamped in the inclined position shown. An Erlenmeyer flask is placed over the upper end. The rest of the apparatus explains itself. (See Fig. 18.)

The gas burns at the jet; the vapor of the liquid is carried up by the draft, and is condensed on the walls of the Erlenmeyer flask, whence it drips into the beaker.

It appears, then, that we are dealing with an effect which is not microscopic at all.

Can we get any idea of the relation which this liquid bears to the gas that is burning? Are they, can they be, the same thing? How can we tell? How can we tell, in general, whether two substances are simply different portions of the same thing or not? In attempting to answer such questions we rely considerably upon what we call the *specific properties* of the substance; that is, those properties which belong especially to the substance in question. If, for example, we are attempting to prove that a given substance is water, we endeavor to show that its properties and behavior conform to the known properties and behavior of water. So also with any other substance we attempt to identify. If, on examination, it presents features which suggest some substance with which we are already acquainted, we follow this hint, and attempt to compare it in other respects, until the evidence seems sufficient. Experience teaches us that it is not usually necessary to compare it in every single respect. If we make careful comparison with reference to two or three of its leading characteristics, our conclusion will generally be trustworthy. For example, if we were given a transparent solid substance which melted at 0° to a colorless, odorless liquid which boiled at 100°, we should be safe in pronouncing the liquid water, and the solid, ice. No one of these determinations alone would be conclusive, but the combination presents exceedingly strong evidence. Again, mercury, such as we have used in our thermometers, is sufficiently characterized by its brilliant lustre, by its remaining liquid at ordinary temperatures, and by its high specific gravity (it is 13.59 times

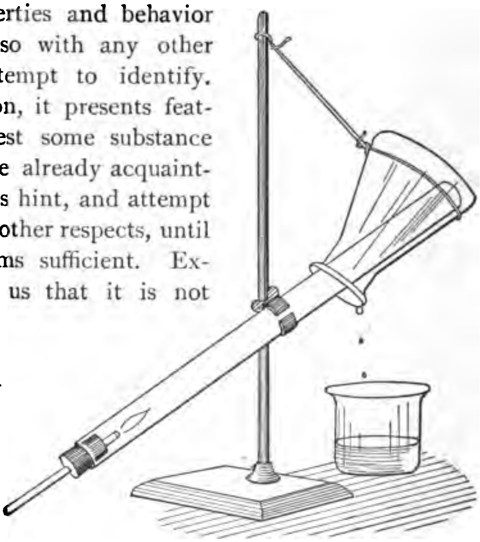

FIG. 18.

as heavy as water). A substance possessing these properties can hardly be anything else than mercury ; and if we can add that it freezes and boils at the same temperatures that mercury does, the evidence is as strong as we could ask.

Now, in the case we are considering, this substance which, at ordinary temperatures, is a gas passes through the tube till it comes to the jet. Here at the jet is this little flame, and beyond the flame a substance appears, which, as soon as it is away from the flame, shows itself to be *a liquid at ordinary temperatures.* It would be contrary to all we have succeeded in finding out about the relations of solids, liquids, and gases to each other to conclude that the liquid is the same substance as the original gas. It seems clear that it cannot be. Moreover, when this liquid is boiled, the vapor which forms condenses on the cooler parts of the tube just the same as before, and a match at the mouth of the tube is extinguished. In view of these facts it seems certain that the liquid which appears when this gas burns in the air *is a different substance from the gas.* There is, however, another line of investigation, which will make our results still more sure, and lead us to new ideas. We are dealing here with a question which is a good representative of the questions with which the chemist is confronted ; and in undertaking to answer such questions it is necessary to cling rigidly to strictly experimental evidence. Now we cannot experiment with forms of matter which have no weight, or with quantities of matter too small for our balances to detect. It is true that by leaving out of consideration substances (if such there be) which cannot be weighed, we limit ourselves; but the limitation is an honest and sensible one, and our results are, at least, consistent. We therefore decide whether anything has been added to or taken from a given mass of matter by weighing it. If it has gained in weight we say it has gained matter. If it has lost weight, it has parted with matter. Now let us come back to our problem from this new point of view. Suppose we arrange our apparatus so that we can put it on the balance-pan, and also so that we can keep the liquid that appears from escaping. If now we start up the flame and let it burn for some time, then either one of three things may be found to be true: the balance may not change: it may show that there has been a gain in weight; or it may show a loss in weight.

The apparatus we will use in investigating this point consists of a 300-c.c. Erlenmeyer flask which serves as a generator, and which has a drying-tube* attached. A flexible rubber tube conveys the gas round to a little pipe-clay jet which is fixed by means of a channelled cork, in the lower end of the inclined piece of combustion-tubing. The rest of the apparatus is like the one we have just employed to condense the liquid. (See Fig. 19.)

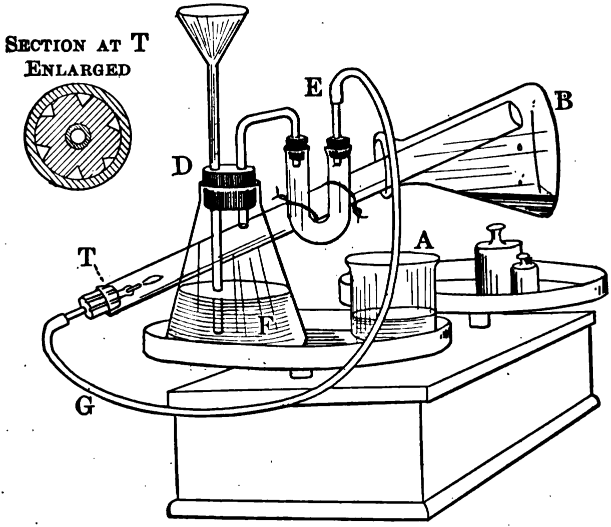

FIG. 19.

The generating-flask with its connections is first placed upon the balance-pan. The zinc is placed in the flask; the acid is kept in a beaker or a flask which stands on the balance-pan while the apparatus is being counterpoised. After establishing equilibrium, the cork carrying the jet is removed from the end of the tube, the acid is put into the generator, and the evolution of gas is allowed to go on until all air has been swept out. The jet is then lighted and put in position. The pointer of the platform-balance is pieced out with a piece of very fine glass tubing (made by heating a piece of soft glass tubing in the flame, and then drawing it out to a fine thread). A piece of paper with a scale upon it, back of the long pointer, makes it easy to follow the movements of the pointer.

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* Calcic chloride.

It appears that a given weight of this gas, in burning, *becomes heavier* or takes to itself some additional matter,* so that the liquid is not the same matter with which we started. This result is in accord with our observation that the liquid which resulted from the burning appeared to be essentially different from the unburned gas; and this last experiment shows us in what respect it is different: *it is the original gas with something added to it.* Before we go on to investigate this matter farther, perhaps it will be well to try some other cases of burning, and see whether the same thing appears to be true. We shall do well to select substances which give solids on burning, for it will then be much easier to collect and weigh the product.

LABORATORY WORK.

Begin by weighing or counterpoising your porcelain crucible, which has been charged with about five grams of iron in fine powder. In most of the cases we are now investigating the "burning" takes place without the production of a flame. The material simply glows, and the glow spreads gradually through the whole mass. Accordingly, after counterpoising, support the crucible on its pipe-clay triangle and heat it over the lamp until the contents begin to glow. Then remove the lamp and let it go by itself. Finally allow the crucible to cool, and reweigh. In some cases the solid formed in the burning is easily carried up and away by the current of hot air. It will perhaps be best to try heating a very little on a piece of asbestos paper first, and see how it behaves. If it seems likely to give trouble, as suggested above, it can be heated with crucible-cover on, the cover being lifted a little from time to time to allow air to get in.

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* Notice that this result is reached even in face of the fact that all the liquid is not condensed, and that some escapes, as can occasionally be seen during the experiment.

Experiment, now, carefully with

Zinc (fine dust),
Copper (filings or turnings),
Magnesium (ribbon or powder),
Lead.

Some cases present particular difficulty. For example, if we recall how phosphorus burns, with torrents of white smoke rushing up from it, we see that here it would not be easy to keep the product from escaping. It can, however, be done to a considerable extent quite easily and without much apparatus.

Place in one pan of your balance your evaporating-dish. Set into it your porcelain crucible in which has been placed a piece of red phosphorus the size of a large pea. Pour a little water into the evaporating-dish (not quite enough to float the crucible). Next set down over the crucible an inverted funnel the inside of which is wet. The stem should be *very loosely* plugged with cotton-wool. Counterpoise the whole apparatus. Then raise the funnel, light the phosphorus with a hot glass rod or a hot wire, and put back the funnel. The burning will go on quietly and regularly, and most of the white smoke will be condensed, or else dissolved by the water. The funnel must be lifted a little occasionally to allow fresh air to enter. If the phosphorus goes out prematurely, allow the whole thing to stand until the smoke has mostly settled, and then light it again. Notice from time to time the state of the counterpoise.

LECTURE 16.

IN the last lecture we saw that when a certain gas was burned in the air, a product was obtained which differed from the original gas in its physical properties, and also in that it weighed more than the original gas. We have also seen, in the laboratory, that other substances when burned in the air give results of a similar nature.

Let us now turn our attention to a line of investigation suggested by one of the experiments made in the course of your laboratory work. Here is a flame which consists of the same gas we have been experimenting with all the time, burning in the air. We seem to have found by our experiments that one thing that happens in the burning is that the *gas gains in weight*, or takes something to itself. From whence does it take this "something"?

In the case of this flame, as it stands before you, it is hard to see any place from whence it could come except *from the air*. At all events, there is an easy way of testing the matter by experiment.

If, when this gas burns in the air, something is taken from the air, and if the product of the burning is a liquid, as we have seen, then if we allow the gas to burn in a confined body of air, under such conditions that we can notice any change in volume, there ought to be a distinct loss of volume.

We can easily meet these conditions in the following manner (see Fig. 20): We lower an inverted jar (containing, of course, air) over the flame which is about two inches or so above the surface of the water contained in a large crystallizing-dish. When the edge of the jar touches the water all communication with the outside air is cut off, and we have our flame burning in a confined body of air. Now if there is loss of volume—that is, if some of the air in that jar is being absorbed by the burning, and is entering into the constitution of the liquid which we know is forming at the jet—then there will presently be a "partial vacuum" formed in the jar into which water will rise to fill the vacancy—and you see it does;—but notice that the flame has now *gone out*, although only a little of the air seems to have been used. It will be well not to attach too much importance to this observation until we have repeated the experiment and verified our results. The same result is, however, obtained every time. All we can say is that in a general way our predictions are confirmed, and it does appear that something is taken from the air. But it also appears that the flame only burns for a limited time, and then ceases to remove matter from the air. Why? Is it because the vapor of the liquid which is formed puts out the flame? Let us test this point. Here is another jar in which just the same thing has been done; that is, the flame has burned in it as long as it would, and then gone out. The jar has been standing for some time, and certainly most of

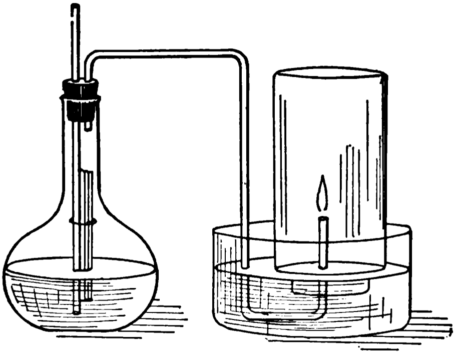


FIG. 20.

the liquid must have condensed. Let us now transfer a little of what is left in the jar to a smaller bottle, and lower this over the flame. It will be seen that the flame cannot exist for an instant. It is immediately extinguished. The experiment is not, however, wholly convincing; and it may be well to try the same experiment with some other substances, which, in burning, do not yield liquids.

Let us try phosphorus. We can easily make the experiment by floating the phosphorus on the water in a little porcelain dish, lighting it, and then lowering the jar over it. You see we have decidedly the same order of result. The water rises to very nearly the same extent as before. You can also see that at the first the burning is quite rapid, and the rapid heating of the air in the jar causes it to expand, so that some of it bubbles out under the edge of the jar. This has a tendency to make the water rise higher in the jar than it would if there were no escape. On the other hand, the flame of the *gas* burning in the jar would, if anything, tend to go out before it had taken the very last bit it might from the air. So that in a rough way we can see that the two experiments tell the same story so far.

Let us now start some more phosphorus ; only this time let us lower over it a jar to which has been transferred some of the gas left in the large jar after the phosphorus had burnt in it. You see the result is the same : the phosphorus will not burn in it.

We could easily multiply experiments upon this point, but it is not worth while at present. It will, however, be of interest to follow the fortunes of a candle when burned in a confined volume of air, for there is a peculiarity about the product of the burning which we have not encountered in our other experiments.

As the candle burns under this dry jar, you see by the dewing over of the glass that some liquid is formed. Soon the water rises as in the former experiments, and our result looks much the same as in previous cases. But now let us repeat the experiment, only letting the lower edge of the jar be sealed by *mercury*, contained in this crystallizing-dish, instead of by water. You see that there is far less shrinkage; yet the glass dews over; and in time the candle goes out as before. If we now pour a layer of water over the mercury in the dish, and lift the jar until it is sealed by water, instead of by mercury, the shrinkage takes place quite quickly; and the result is practically the same as in the other cases. This seems to show that besides the liquid there is a gas formed when the candle burns, and that this gas is dissolved by water. This is, as a matter of fact, the case.

We have seen that when sulphur burns in the air, a gas with a choking odor appears. This gas is also soluble in water. It is, therefore, possible to burn sulphur in a jar of air standing over water, and to show that here, too, we arrive at substantially the same result as in the other cases; namely, that, in the burning, a certain portion of the air is used up, and that in the remaining portion of the air none of these substances can be made to burn. Moreover, since we have seen that in all these cases there is increase in weight, it is now clear that the product which appears as the result of the burning consists of the original material plus something it has taken from the air. Furthermore, it seems clear that in the air we must recognize at least two distinct gases, namely, one which is taken up by burning substances, and one in which ordinary substances refuse to burn.

Before we go on to investigate this matter more carefully, let us take a little more extended survey of this action of the air upon different substances. We have already seen that a number of substances, when heated sufficiently hot in the air, *burn*; and that the burning is sometimes accompanied with flame, and sometimes not. Charcoal burning without perceptible flame is consumed in time, and experiment shows that there is the same effect produced upon the air in which it burns as when it burns more violently. Again, iron and others of the common metals *rust* in contact with the air; and the rusting, if performed under the same conditions as in our other experiments, will show the same shrinkage as we have observed in the other cases. This you can presently see for yourselves in the laboratory. Phosphorus *rusts* in contact with the air also, and with considerable rapidity. Some substances show no perceptible change, no matter how long they are left in contact with the air at ordinary temperatures. Sulphur is such a substance, and there are a number of others.

LABORATORY WORK.

Let us try to determine pretty carefully just how much shrinkage there is when substances burn or rust in the air. We will try three methods, and see how the results compare.

1. The graduated cylinder should be clamped securely with its mouth downward, and dipping under the surface of the water in the pneumatic trough, in such a way that a volume of about 100 c.c. of air is confined (see Fig. 21). This volume should be carefully observed and recorded. A piece of ordinary (yellow) phosphorus should now be stuck on the end of a piece of copper wire (under water), and the wire carrying the phosphorus should be brought up into the air-space in the graduate and allowed to remain for several hours. Care should be taken that the phosphorus does not touch the sides of the tube, and that it stands

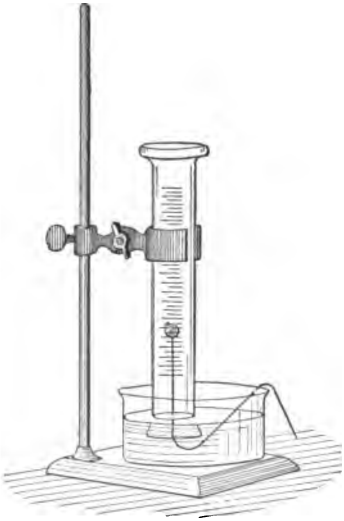


FIG. 21.

well up toward the top portion of the graduate. Return your result in form of a percentage; that is, state the percentage of the air which disappears during the burning.

If graduated cylinders are not available, test-tubes will answer very well. In this case the levels of the water before and after are marked on the test-tube by means of thread, or rubber bands; and the volumes are measured by determining the weight of water required to fill each of the spaces in question.

2. For a second method a small retort, the bowl of which contains moist iron-filings, is inverted over the trough, or in a fruit-jar of water, mouth downward, so as to enclose a carefully marked volume of air. Allow it to stand overnight, and measure volumes as in the previous experiment.

3. Thirdly, use the candle-flame. A short length of a small wax candle should be secured, by means of a drop of wax or Canada balsam, to the bottom of an evaporating-dish, saucer, or crystallizing-dish containing a little water. A suitable wide-mouthed bottle should now be brought down over the lighted candle, so that its mouth is sealed by the water. (See Fig. 22.) When the candle goes out, the bottle should be carefully shaken from side to side without removing from the dish; and this should be continued until there is no further decrease in volume. The volumes can now be measured by whatever method is most convenient.

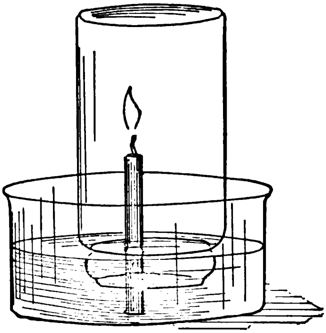


FIG. 22.

LECTURE 17.

We have now arrived at the point where we can intelligently, and with considerable confidence, regard the burning of this gas in air as a sort of union of the gas and part of the air, to form a liquid which is distinctly a new product. Now if this is so, if it is simply a question of the gas and air being brought in contact and heated to the temperature at which they burn together, or unite, then it ought to make no difference whether we light a jet of the gas flowing out into the air, or whether we light a jet of air flowing out into an atmosphere of the gas. The idea of burning air is, at first sight, a curious one; but we are in a position to look at it now not only as a possibility, but as a strong probability; and it will be well worth while to see if we cannot devise some method of submitting the matter to experiment.

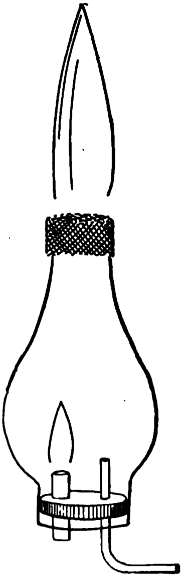


Fig. 23.

Here is a very simple piece of apparatus which will serve our purpose very well (see Fig. 23). It consists of an ordinary lamp-chimney the upper end of which is covered with a cap of fine copper gauze. The lower end is closed with a rather thin cork through which enter two tubes. One of these is short, only about $\frac{3}{4}$ of an inch long, and about $\frac{1}{4}$ of an inch internal diameter; the other is rather slenderer and longer. Now in putting this apparatus into operation, we will use, instead of the gas we have under study, ordinary illuminating-gas, simply because it is more convenient. There is no difference in their bearing upon the point we are investigating.

We first connect the slender tube at the base of the lamp-chimney with the gas-supply; allow it to run full pressure for a few seconds; then turn it down somewhat, and light the illuminating-gas at the top of the chimney, so as to make a flame about 5 inches high. Now the interior of the lamp-chimney is full of illuminating-gas; and the up-draft created by the flame is drawing air in through the wide tube in the cork at the base. If now we push a lighted match up through this tube, the *jet of air takes fire* and burns in the atmosphere of illuminating-gas. Moreover, so far as the eye can detect, there is little difference between this and the burning of illuminating-gas in air. You see the wall of the lamp-chimney is dimmed over in this case as well as in the other.

It appears, then, that we can burn illuminating-gas in air, or air in illuminating-gas. The same thing can be done with air and any other gas which burns in it. Of course some experiments of this class will prove less convenient than others. For example, we can burn air in an atmosphere of our light gas, if we wish; but the difficulty here is, especially if we use an apparatus of this size, that it takes a rather large generator to supply the gas for the large flame which burns at the top of the lamp-chimney; but this difficulty can of course be met if it seems worth while; and the same is true of all similar cases. Perhaps you will agree, however, that the main point has been sufficiently well established by this one experiment; and we will accordingly direct our attention to a question suggested by these studies of ours. We have seen that, in the act of burning, our light gas and the air—or part of it, at least—go together and form a liquid. Now do they go together in any particular volume proportions? This is an entirely natural question. When we see the flame burning in the jar of air, over water, and when we see the water rise into the jar, which means that a certain portion of the air has been taken up by the gas in burning, we can hardly fail to raise the question whether in using up this fraction of the air in the jar (which, as we have found, is about one fifth) any definite volume of the light gas has been burned.

It is not difficult to think out a way of roughly testing the matter. The main condition we must meet is this: We must have some source of the light gas, such that we can measure the amount used in burning out the fifth part of a jar of air. It is, of course, easy to determine the volume of gas which has been taken from the air, and so we have the answer to our question. (See Fig. 24.) Here are two large bottles. One of them has a hole bored in it near the bottom, and in it is fixed, by means of a short sleeve of rubber tubing, a piece of glass tubing, which, in turn, is connected, by means of flexible rubber tubing, with a glass tube passing through one of the holes in the stopper of the lower bottle, and dipping very nearly to the bottom of it. Through the second hole in the same stopper

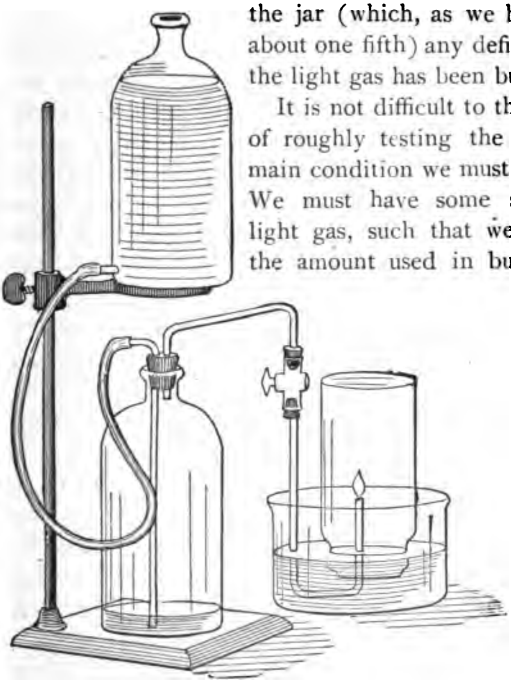


FIG. 24.

comes a tube which is bent in form of a delivery-tube and terminates in a pipe-clay jet. Midway in this tube there is a short length of rubber tube carrying a pinch-cock. The lower bottle has been filled with the light gas by the following manipulation: First, the lower bottle was entirely filled with water. Next, the delivery-tube was connected with a generator yielding the light gas, and the upper bottle was temporarily lowered. The pressure of the entering gas forced the water from the lower into the upper bottle. The current of gas was allowed to flow until the water was nearly all expelled from the lower bottle and replaced by gas. The pinch-cock was then closed, and the generator disconnected. The upper bottle was then raised to its present position. We have now, confined in the lower bottle, some of the light gas. We will now lower the upper bottle until the levels of water in the two bottles coincide. This is to make sure that the gas in the lower bottle is at atmospheric pressure. We now carefully mark, by a fine rubber band, the level at which the water stands now in the lower bottle. Next, we raise the upper bottle again and open the pinch-cock slightly, light the jet and immediately lower the jar over the flame. The water rises into the jar, as usual, and presently the flame goes out, whereupon the pinch-cock is at once closed. Next we bring down the upper bottle until the levels again coincide, and slip another rubber band down over the lower bottle to mark the new level. Now clearly the volume represented by the space between these two bands represents the volume of light gas which has been used, and we can easily measure its amount. In the same way, by slipping a rubber band down over the jar to mark the level to which the water has risen, we know that the volume represented by the space between the rubber band and the mouth of the jar represents the volume of what has come from the air. We now measure these two volumes by filling them from a graduated cylinder. One represents the volume of light gas; the other represents the volume of gas taken from the air in the burning of this volume of the light gas. On comparing them, we see that the volume of the light gas is roughly twice that of the gas taken from the air.

This experiment is an interesting one and very simple in principle; but clearly it is not capable of yielding very sharp results. In the first place, the measurement of volumes is rough and inaccurate. This might be remedied. In the second place, it is difficult to manage so that the jar is lowered over the flame the very instant it ignites; and a similar difficulty turns up at the end of the experiment, when we come to shut the pinch-cock the instant the flame goes out. Let us then try to study out a different method. Our first step shall be to make the acquaintance of a method of burning which is different from any we have yet studied. In the case of our light gas, the only way we have ever seen it burn is at the jet, as a quiet flame fed by a continuous stream of the gas. The reason why it only burns at the mouth of the jet is now clear to us. It is because that is the first point where it comes in contact with air. But suppose now we take a test-tube and mix up in it some of the light gas with air, and then apply a match to the mouth of the tube; as things are now the gas is *everywhere in contact with air*, and it seems natural to expect that the burning, once started in the vicinity of the match, would be rapidly transmitted throughout the whole contents of the test-tube. We should thus have a very rapid burning.

On trying the experiment, we find our predictions fulfilled. The burning is so rapid that it amounts to a slight explosion. The inner walls of the test-tube were dry. You now see that there is the same dewing over of the walls of the tube as in the other cases. It thus seems probable that the general nature of the burning in this case is the same as in the others. If now this slight explosion is the outward manifestation of the forming of the liquid, by the union of the light gas and the gas obtained from the air, then it follows that the more liquid formed, the louder the explosion. And if we take a test-tube like this one and experiment with different mixtures of the light gas and air, we ought to be able to arrive at a certain mixture which gives a louder explosion than we get with any other. Now when we find this point, that is, when we have found how much light gas and how much air to mix in order to get the loudest explosion possible in that sized test-tube, a moment's reflection will show that the gas and air must be mixed in such proportions that there is exactly the right quantity of air to just consume the light gas present in the tube (see Fig. 25). For suppose the test-tube shown in the figure to be divided by a thread; and suppose that the light gas and air are in the proportions shown; and further, that these proportions give the loudest explosion. We are evidently forming the largest amount of liquid we can in a tube of that capacity; and since the amount of liquid formed depends upon the amount of light gas burned, it follows that in the tube there must be such proportions of the two gases that the light gas will be just consumed by the air that fills the rest of the tube. If a larger proportion of the light gas is taken, this necessarily cuts down the amount of air. As a result, all the light gas will not be burned, and less liquid will be formed. If we decrease the amount of light gas, we of course decrease the amount of liquid formed. So if we can manage to find the mixture that gives the loudest report, and if we know the relative volumes of air and the light gas, we can easily get at the relative proportions of the light gas and that part of the air which is used in the burning.

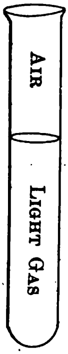


FIG. 25.

LABORATORY WORK.

In order to fill a test-tube with a mixture of the light gas and air, proceed as follows: Suppose the mixture is to consist of equal parts of the two gases. Fill the test-tube half full of water. Cover with the thumb and invert. Place with the mouth dipping under water, mark the boundary-line between air and water by a bit of thread, and remove the thumb. The tube is now half full of air; and the requisite amount of gas can be added from the generator at the rate of about four bubbles per second. The instant the tube is full the generator delivery-tube should be taken away.

These details being mastered, fill three test-tubes: one with much air and little light gas; one with much light gas and little air; and the third with about equal parts; marking with threads in each case. The three tubes should now be successively removed from the trough (closing the mouth of the tube carefully with the thumb), and exploded by bringing them to the Bunsen flame in the position shown (see Fig. 26). Notice which gives the loudest report. (By 'loudest' is meant, not the roundest and fullest sound, but the sharpest and most piercing one.) Take the test-tubes again, and make three more trials; using in one a little more air, in the other a little less, and in the third the same amount as was used in the test-tube giving the loudest report. Keep up this process till you finally find a point at which the report is sharper than at any other point. When this is done, wipe out the test-tube and fill the spaces representing air and light gas successively from a burette or a graduated cylinder, noting carefully the volumes in cubic centimeters. Calculate now the ratio between the volume of light gas burned and that of the gas used from the air; remembering that one fifth of the air only is used by the light gas.

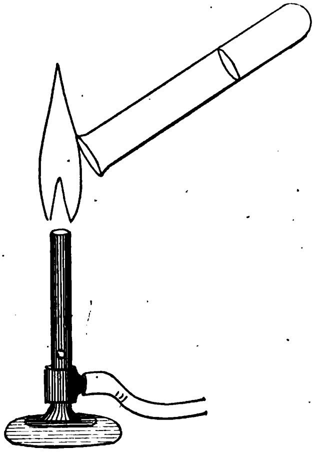


FIG. 26.

In recording this ratio, remember that it is customary to make the smaller quantity 1, and see what the other one becomes. For example, if the two volumes were 3 and 9 cubic centimeters, the ratio between them is as 1 to 3.

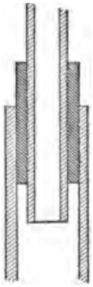
LECTURE 18.

THUS far we have confined our attention almost wholly to the nature of the act of burning, as exemplified in the burning, in air, of what we have up to this time called "the light gas." It has not been necessary, and for some reasons would not have been best, to concentrate attention upon the individual actors in the scene. We have been concerned simply with the parts played by each of them in the burning process. Now, however, it will be advantageous, for reasons which will soon appear, to gain some more particular knowledge of the three individual substances concerned.

To begin with, then, the liquid which results when the light gas is burned in air is none other than water. The proof is simple and decisive. It is impossible to detect any difference between the liquid as thus produced and the substance we call pure water. It has the same density, freezes at the same temperature, boils at the same temperature, has the same rate of expansion, increases in bulk in the act of freezing, is odorless, tasteless, and colorless as ordinarily viewed.

It follows, then, from our experiments, that our light gas is one of the constituents of ordinary water. This light gas is called *hydrogen*. Its name is of Greek derivation and means *water-former*, and we can now see the appropriateness of the name. It is well worthy of note, however, that the fact of the gas now having a name adds nothing to our knowledge of it. The name is simply a matter of convenience. Another constituent of water is the gas taken from the air in the act of burning. We say *another* constituent and not *the other*, because we have, so far, no right to conclude that these are the only constituents. We have not yet put on the final and crucial test. We have not actually weighed the gases which combine in the act of burning, and proved that in forming water there is no loss or gain of the original quantity of matter represented in the mixture. It is, however, certain that the two gases are present in water, and in the proportions of two volumes of hydrogen and one volume of the gas taken from the air; which gas we now proceed to study a little by itself.

First of all, how can we isolate it? We have thus far met with it only in the air, where it is mixed with about four times its bulk of another gas, as our experiments have shown. We have, however, removed it from the air at various times; sometimes in combination with hydrogen, as water, sometimes in combination with other substances, such as zinc, iron, sulphur, or phosphorus. Is it not possible that by some means or other we may succeed in causing some substance which has taken up this gas from the air to give it up again? On following out experimentally the line of inquiry thus suggested, it is found that there are a few substances which fulfil the required conditions. The easiest one to experiment with is the substance obtained by heating mercury in contact with the air. The formation of the substance by the actual heating of mercury in the air is not a practicable experiment for the lecture-table, as it is a rather slow process; but here is some of the substance after it is made.


FIG, 27.

Now this substance on heating* certainly yields a gas, as will be shown presently, and that is promising.

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* A piece of hard glass tubing about 6 inches long and ¼ inch internal diameter should be sealed at one end and charged with a few grams of the mercury compound. The other end should be connected with a delivery-tube by means of a short sleeve of rubber tubing as shown in Fig. 27. The gas should be collected over water.

When the red substance is heated in this tube, two things happen, both of which can be watched by any one standing near the apparatus. The only one you can readily see is the evolution of a gas which collects in the cylinder over water.

The other effect, namely, the appearance on the cooler portions of the inner walls of the tube of little globules of mercury, is equally significant. We have now collected sufficient of the gas to examine; but before we do anything with it, let us see what sort of properties we should be inclined to ascribe to it in advance, and then see how our predictions are fulfilled.

If this is the same gas that is in the air, it exists there mixed with about four times its volume of a gas which seems to play no part in ordinary burning. The natural effect of this condition of things would be to lessen the rapidity with which the active gas enters into combination with hot substances, and it follows that if the gas could be isolated and obtained pure, substances ought to burn in it the same as in air, only more rapidly and violently. Let us now try the burning of a match in a test-tube full of the gas.

You see how much more decided it is than when it takes place in the air. Indeed, if we blow out the flame of the match, and leave only this glowing coal on the end of it, you see that on plunging it into another test-tube full of the gas we have obtained, the coal actually bursts into flame. Here is some powdered charcoal which has been heated red-hot in an iron spoon. You see how brilliantly it burns when sifted into a tube containing the gas. On lowering this test-tube full of the gas over a hydrogen-flame water is formed. Everything seems to show that we are on the right track.

It would, however, be very desirable to get similar results with some other substances. Now the one with which we have had the most to do is water; but it is not practicable to do with water as we have with the mercury compound.

There is, however, another kind of force which can be brought into play, by which we can get better results.

When a galvanic current is passed through water to which a little dilute sulphuric acid has been added, the effect is very striking, and appeals to the eye more than does the last experiment;* for when the circuit is closed there is a brisk evolution of gas at each electrode. The apparatus has been in operation for a while already, and you see we have collected in each of the test-tubes at the delivery-tubes some gas. Our recent work gives us every reason to anticipate that these are hydrogen and the other gas which we have seen to be

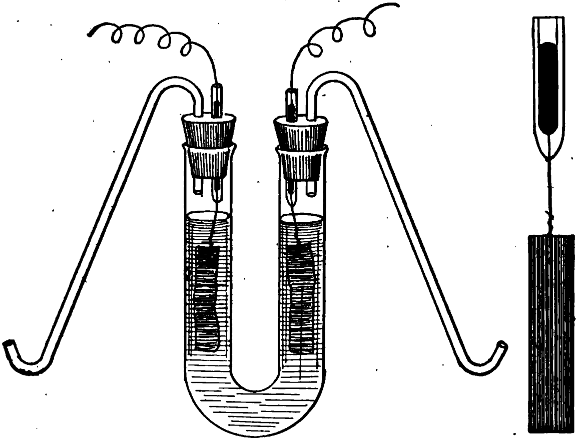

FIG. 28.

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* A very simple and serviceable decomposing cell is shown in the figure. For the most part it explains itself. The electrodes are platinum foil. To each electrode is attached a small piece of platinum wire which is simply threaded through the electrode by means of a pin-hole. The short lengths of wire are fused into the little tubes which enter through holes in the stoppers. These little tubes are filled with mercury and serve to establish connection with the battery, which may conveniently consist of five dipping Grenet cells. The mercury-cups will be understood easily from the following detail sketch.

present in water. Moreover, we are in a position to say which is which, for we have seen that the hydrogen and the other gas are present in water in the proportions of about 2 to 1. Now these two gases are certainly evolved in proportions which are very nearly 2 to 1, so we may confidently predict that this tube, which contains the larger amount, will turn out to be hydrogen. You see that on bringing the mouth of the test-tube containing it near a flame its behavior is the customary behavior of hydrogen. In view of the circumstances, further proof may be dispensed with for the present. In the same way we can satisfy ourselves that the other gas shows the same behavior as that obtained from the mercury compound. A single experiment with the coal of a match, in which we get the same result as in the other case, makes it extremely probable, *in view of the circumstances*, that we are dealing with the same gas in the two cases. We have, then, apparently succeeded in isolating that gaseous constituent of the air which enters into combination with burning substances. Finally, it is worth noticing that the gas prepared from potassic chlorate and manganese dioxide, and which was the very first one we experimented with, is identical with the gas from either of the above sources. The most careful scrutiny fails to detect any difference. This is important, for it gives us a cheap and easy way of preparing the gas whenever we wish to use it in the laboratory. It is called *oxygen*. Its name means *acid-former*, but this has little significance for us at present.

We have now studied out in considerable detail the relations of hydrogen, oxygen, air, and water to each other, and have gained some quite definite ideas as to the nature of such processes as burning, rusting, etc. Our investigations on these points have involved absolutely no assumptions, and the results we have obtained, as we will now sum them up, must be regarded as final and immutable. We have shown:

1. That air contains at least two gases.

2. That one of these, which we call oxygen, and which is present to the extent of about one fifth the total bulk, is the substance which is responsible for what we call the *burning* of substances in contact with the air; and that burning consists in the union of oxygen with the burning substance, either wholly or in part.

3. That the gaseous residue left when oxygen is removed from ordinary air plays no part in burning, but acts to dilute the oxygen, and thus weaken its action.

4. That when hydrogen burns in the air, at a jet, or when it is mixed with air and the mixture exploded, the hydrogen unites with oxygen in proportions which are very closely two to one *by volume.*

5. That under the circumstances stated above, the hydrogen and oxygen unite in weight proportions which are very nearly as one to eight; for we have found that they unite in the proportion of two volumes of hydrogen and one of oxygen; and since, as we have determined, a given volume of oxygen weighs about 16 times as much as the same volume of hydrogen under the same conditions, it follows that the ratio between the weight of two volumes of hydrogen and one of oxygen will be as *one to eight.*

It seems very probable that these two substances are the only constituents of water; but it will be more satisfactory if we can test this matter by direct experiment. We must contrive some apparatus which will enable us to weigh the hydrogen used, the oxygen used, and the water formed. If we can do this, and if the sum of the weights of hydrogen and oxygen are found to be equal to the weight of the water formed, we are warranted in concluding that water is composed of hydrogen and oxygen alone.

LABORATORY WORK.

Set up a piece of apparatus as figured (see Fig. 29). Tube *A* is a piece of hard glass tubing (arsenic tubing) about one fourth of an inch internal diameter and 7 inches long. It should be carefully cleaned, and then drawn down to smaller size at one end so as to go easily through the stopper of the tube *B*. It should project downward from the lower face of the stopper for about half an inch. Its other end is to be connected with the short bent tube coming from tube *C*. This is done as follows (see Fig. 29):

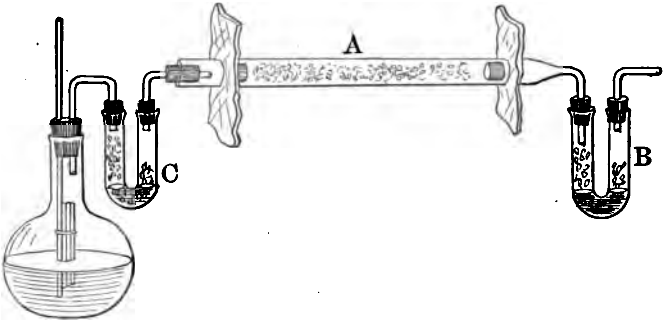

FIG. 29.

The rough edge of tube *A* should first be "fire-polished." A piece of smooth rubber tubing is then inserted for about one fourth of an inch and the end of the small glass connecting-tube is pushed through till it projects a little on the other side. The joint should be so tight that when the small tube is in place it can be twisted only with some difficulty. While this tube is being thus fitted up, some *granulated* cupric oxide should be heated to dull redness in a small iron crucible over the Bunsen flame, and allowed to cool.

The tube *A* is now to be filled with this material; which will be held in place by two little plugs made by rolling up a strip of asbestos paper about one fourth of an inch wide into a loose spiral, which will go into tube *A*. Care should be taken that the plugs are loose, and that they leave plenty of openings so that the passage of gas through the tube will not be obstructed. They should be heated to redness before being put in place. The U tubes are both charged with glass beads and sulphuric acid (strong). In each one the beads should fill about the whole of the first limb and about half the second. The acid should just seal the bend. See that the beads are thoroughly wetted by the acid.

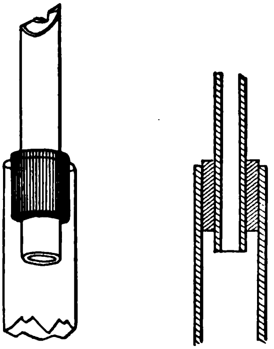
FIG. 30.

All stoppers are rubber ones, and carefully fitted to their places.

Everything being satisfactorily put together, the determination is made as follows:

1. Charge the *dry* tube *A* with the still warm cupric oxide.

2. *When the tube feels cool to the touch* make the following weighings with all possible care; making sure, in each case, that everything is clean and dry:

(1) Tube *A* alone (it is best to draw the end of tube *A* from the stopper of tube *B*; and the same is true at the other end).

(2) Tube *B* alone with its stoppers and the short exit-tube.

3. Tubes *A* and *B* together.

4. See that the generator is giving hydrogen free from air. Connect it to tube *C* and allow a slow stream of hydrogen to flow through the apparatus (the bubbles should pass the U tubes at the rate of about three per second), until a test-tube full of the gas caught at the outlet of tube *B* proves free from air. Then begin heating the cupric oxide in tube *A*, at the end nearest the generator. In order to protect the stoppers from accidental overheating, it is well to put asbestos-paper screens on the tube at the plugs, as shown. The back end of the cupric oxide should be heated until it is dull red-hot; but *care must be taken that the whole length of tube* A *is kept hot*; or the water may condense in the oxide, and when the flame strikes that portion of the tube where the oxide is wet, it will almost certainly crack. Keep up the heating until the entire contents of tube *A* have changed color from black to red.

5. Allow the whole apparatus to cool thoroughly, keeping up the current of hydrogen. When it feels cool to the hand, disconnect the generator again. Make the same weighings as before.

It is now clear that

weight of tube A before − weight of tube A after = oxygen used;
weight of tube A after − weight of tube B before = water formed;

and

(wt. A + wt. B) after − (wt. A + wt. B) before = hydrogen used.

The results should be given under the following headings:

Hydrogen Weighed.	Oxygen Weighed.	Water Weighed.	Ratio Hydrogen to Oxygen.
(............)	(............)	(............)	(............)

LECTURE 19.

BEFORE we finally sum up and discuss the results we have thus far reached in our study of the relations of hydrogen, oxygen, and water to each other, one final question suggests itself. We have seen that when these two gases unite to form water they unite in proportions by volume which are very closely as two to one. Now suppose the experiment to be performed at such a temperature that the water which is formed *remains gaseous*. What then will be the volume of *gaseous* water formed by the union of the two volumes of hydrogen with the one volume of oxygen?

In order to meet these conditions, it is clearly necessary that the combined volume of the two gases when mixed ready for explosion, as well as the volume of the resulting steam, must be observed at a temperature at which water remains gaseous; that is, at a temperature above 100°. This can be accomplished without difficulty by means of the apparatus now to be described (see Fig. 31).

The essential feature of this apparatus is the long tube (*A* in the figure) which has two little platinum wires sealed into its upper end in such a way that they come within about $\frac{1}{16}$ of an inch of each other. The object of this is to furnish means by which we may light the mixture of gases which is to be confined in the tube. This is done by connecting these wires with the poles of an induction-coil, and sending an electric spark between the two little wires. The tube thus prepared is jacketed by a larger tube (*B* in the figure). Into the top of this tube steam is led from a flask *C* containing water which is kept boiling by a Bunsen lamp.

The condensed water escapes by the bent tube at the left of the figure. By this means the contents of the inner tube can be kept at 100° as long as we please. The cylinder *D* is of fairly thick glass and contains mercury.

At the beginning of the experiment the inner tube is carefully cleaned and dried, filled completely with *dry* mercury, and placed mouth downward in the mercury cistern. We now wish to introduce into this tube hydrogen and oxygen in the proportions of two volumes to one, respectively. To do this, we first lift the inner tube so that its mouth is about half

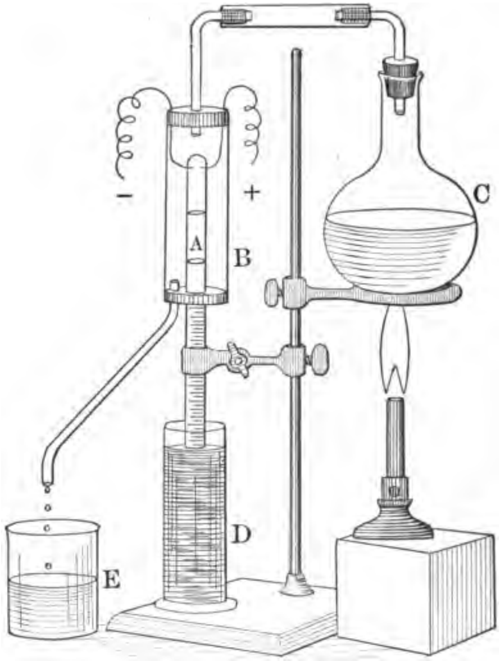

Fig. 31.

an inch under the surface of the mercury. We can then bring under the mouth of the tube the delivery-tube of a hydrogen generator, and allow the gas to bubble up into the tube until two of the divisions marked off on it are filled. We then fill the remaining division with oxygen in the same manner; only the oxygen is drawn from a reservoir containing it, and not from a generator.

Another and simpler way is to decompose water by the current in a little decomposing-cell (see Fig. 32), which is like the one previously used, only there are no separate compartments for the two gases. As a result, we get, at this delivery-tube, the mixture of hydrogen and oxygen just as it comes from the water. We have seen that under these circumstances the gases are produced in the proportion of two volumes of hydrogen to one of oxygen. In using this apparatus, we first fill the three divisions of the tube with the mixture of gases. During this process the steam has been kept circulating, so that we may measure the gases at the temperature at which we shall measure the product. The steam is now stopped; the height of the mercury in the inner tube above that in the cistern is noted; the top stopper of the jacket is removed and the wires connected. Next, the inner tube is lowered so that its mouth is four or five inches under the surface of the mercury, and a spark is caused to pass between the two little wires. The explosion is a sort of mixture of click and jar; and you see the mercury has instantly flashed up to the top of the inner tube, so rapid is the

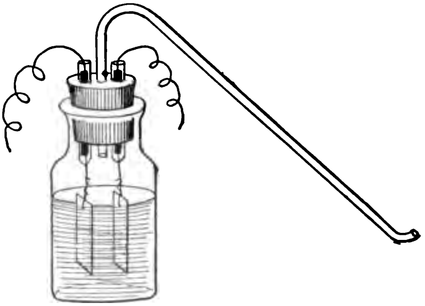

FIG. 32.

condensation of the water vapor. The steam is now started again and the contents of the inner tube are speedily raised to their former temperature. Finally the distance between the levels of mercury in the inner tube and in the cistern is made the same as before the explosion, when the volume of the steam is seen to be *only two thirds that of the mixture before explosion.*

If there had been any extra hydrogen, of course the volume of the resulting product would have been greater than it is now by just the amount of this unused hydrogen. The same would be true of extra oxygen. But whenever we mix the two in just the proportions in which they are present in water, the volume of steam at 100° is always two thirds that of the original hydrogen and oxygen.

We cannot appreciate the full significance of this result without some more data of a similar kind. Unfortunately the number of cases which can be readily handled upon the lecture-table or in the laboratory is very small; and the difficulty of actually experimenting further along this line would be great. The following description of a similar case may be of assistance, however. Oxygen is not the only gas in which hydrogen will burn. There is a gas called *chlorine*, which differs in appearance from oxygen in being greenish yellow, instead of colorless. In this gas hydrogen burns with much the same appearance as it does in air or in oxygen. Our experiments have taught us to look for some product in all such cases, and in this case we are speedily made aware of the nature of the product. It is a *gas* of exceedingly pungent and penetrating odor. It is very soluble in water, and the strong solution is a common reagent in the laboratory, as we shall see later. The union of these two gases has been studied in the same manner as we have just studied the union of hydrogen and oxygen; and the following facts have been established:

1. The two gases unite in the proportion of *one volume*

hydrogen to one volume chlorine. This is proved by lines of experiment exactly parallel to those we have pursued.

2. The combined weights of hydrogen burned and chlorine used are together exactly equal to the weight of the gaseous product of the burning.

As was previously stated, it would be a rather troublesome matter to operate with these two gases in such an explosion apparatus as this. For one thing they have an uncomfortable way of combining explosively under the influence of sunlight; and sometimes this happens in ordinary diffused light. For another thing, chlorine is an exceedingly disagreeable gas to inhale, even in small quantities. Therefore we will imagine the experiment to have been made (as it has, at other times), and consider the results. Suppose two divisions of the inner tube to have been filled with the mixture of the two gases in equal proportions by volume, and the mixture exploded by the spark. On observing the volume of the resulting gaseous product we should find there had been *no change whatever.* Let us sketch these results in a form in which we can study and compare them (Fig. 33). At first sight there seems to be no clearly defined relationship between them; but on looking more closely we see that there is, and it is this: that in both cases the volume of the resulting product is just *twice* the unit of volume. That is, if we had measured out our gases in cubic centimeters, and had taken two cubic centimeters of hydrogen and one of oxygen, the volume of gaseous water would be two cubic centimeters. And if we had taken one cubic centi-

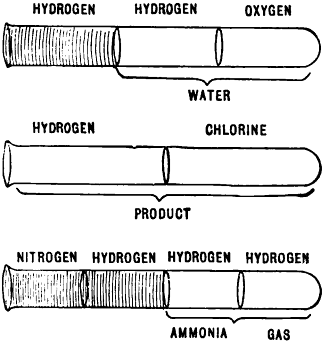

FIG. 33.

meter each of hydrogen and chlorine, we should have as a result two cubic centimeters of the resulting product.

There is still another case which may be mentioned. It is much more complicated and difficult to handle on the lecture-table than either of the other two.

Under certain conditions it is possible to bring hydrogen into combination with nitrogen (which is, as we have seen, one of the gases which air contains in addition to oxygen); and the product is a gas called *ammonia*. It is not practicable to cause the two gases to unite by explosion,* but it is possible to take ammonia-gas and *decompose it*, when the volumes of the two gases obtained can be observed. This can be done by inclosing the ammonia-gas in a tube over mercury, and sending a series of sparks through it from an induction-coil. The volume increases steadily for a while, and then becomes stationary. On examination, it is found that the total volume is twice what it was before, and that it is made up of one fourth nitrogen and three fourths hydrogen by volume. That is, if the total volume *after decomposition* were, say, four cubic centimeters, the volume of nitrogen would be one cubic centimeter, and that of hydrogen three cubic centimeters. And since the volume doubled during the action of the spark, the original volume was evidently two cubic centimeters. That means that *if it were possible to combine nitrogen and hydrogen directly*, and if we mixed one cubic centimeter of nitrogen and three cubic centimeters of hydrogen, we should get as a result *two* cubic centimeters of the resulting gaseous product; so this case is just like the others.

LABORATORY WORK.

Determine for yourself the composition of the compound of hydrogen and chlorine mentioned in the lecture.

First, however, if a good hood is at hand, collect (over strong salt solution) a bottle of chlorine-gas from a suitable generator, and see for yourself that your hydrogen-jet will burn in it. Note *cautiously* the odor of the gas formed by the burning. Next take a little salt and put it in a test-tube. Pour over it a little strong sulphuric acid. Simply note the odor of the escaping gas. Notice, too, how it fumes as it comes in contact with the air. Of course this is not conclusive evidence to you that the gas is the same as that produced by burning hydrogen in chlorine (or chlorine in hydrogen). It is not intended to be. It only brings out one or two of the first observations which lead on to more careful work, by which it is shown that the two substances are the same thing exactly.

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* It is possible, however, to cause nitrogen and hydrogen to unite directly, but not under such conditions that we can observe the volume of the resulting gas.

The determination of the composition of this gas by volume can be arrived at in several ways. In the first place, notice the proportions in which the gases are given off when a water solution of the gas is acted upon by the electric current, in the same little decomposing-cell as was used in case of water.*

Secondly. There are some substances which, when brought into this gas, absorb the chlorine and leave the hydrogen (in the same manner as hydrogen removes the oxygen from cupric oxide). Seal the end of a piece of hard glass tube 6 inches long and about ⅜ inch internal diameter. Bend the sealed end as shown in Fig. 34, the short limb being about 1½ inches long. Over the other end fit *tightly* a smooth piece of fairly thick-walled rubber tubing, having fully an inch bearing on the glass, and provided with a screw pinch-cock as shown. Introduce into the short limb a small piece of metallic aluminum.

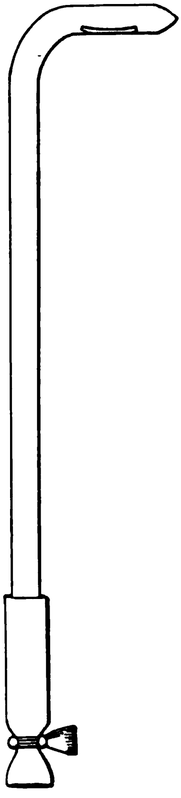
FIG. 34.

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* The positive electrode should be a piece of gas-carbon in this case, as platinum would be attacked by the chlorine. One of the cells can be set up where the whole class can see it.

Next fill the tube with dry hydrogen chloride. To this end heat about 50 cc. of concentrated hydrochloric acid in a 100 cc. flask provided with a sulphuric acid U tube to dry the gas. Lead the delivery-tube well down into the bent tube, *having the pinch-cock in place.* When the air has been thoroughly expelled from the whole apparatus (which will take about five minutes), *slowly* lift out the delivery-tube and *at once* close the pinch-cock. Restore the tube to its upright position, taking care that the little piece of aluminum is in the short limb.

Heat the metal with a Bunsen flame until white clouds begin to rise from it; then heat rather more gently for a few minutes. Cool the tube thoroughly; then place the open end under water, pinching the free end of the rubber tube to expel included air. Open the pinch-cock. The walls of the rubber tube will probably stay together owing to the partial vacuum inside, and it may be necessary to pinch it in such a way as to force the walls apart. If all has been carefully done, the water will rise into the tube and fill the space representing the chlorine, which is now united with the aluminum, the compound formed being a solid at ordinary temperatures, and readily soluble in water. Mark the division-line with a rubber band; then turn the tube so that its mouth is uppermost and bring a lighted match to the mouth. Finally measure the volume occupied by hydrogen and that occupied by chlorine.

A second decomposition of the gas, which is interesting since it enables us to measure the volume of the chlorine, is as follows: About 1 gram manganese dioxide is introduced into the short limb of the apparatus. Next the tube is filled with the gas by the same manipulation as in the last experiment, and the pinch-cock is closed. On warming gently the oxide rapidly oxidizes the hydrogen to water and sets the chlorine free. Open the tube with its mouth under a saturated salt solution and note the shrinkage, which here represents the hydrogen that has disappeared.

A third method, which is a little different in detail from those just given, is as follows: Very thoroughly fill a 100 cc. flask with the gas. Close the mouth of the flask with the thumb and bring it mouth downward into a dish of water. Very cautiously move the thumb a little, when water will rush in. Let about five cubic centimeters of water enter the flask;

then close firmly and shake vigorously for several minutes. We now have the gas in water solution. Adapt a cork and delivery-tube to the flask and arrange a test-tube to collect any evolved gas over water. Drop into the flask a roll of about 3 inches of magnesium ribbon. Quickly replace the stopper and collect the gas in a test-tube or in a graduated cylinder. Let it run until the next period. Satisfy yourself that hydrogen has been collected; measure volumes and see how the results agree with those already obtained.

LECTURE 20.

We have now accumulated quite a body of facts; and we may well stop and survey them quite carefully, before we pass on, for they are a remarkable and interesting collection.

First of all, we seem to have found that water has always the same constitution. At least you have formed water from hydrogen and oxygen a number of times; and so far as your resources will allow you to observe, the result has always been the same. As a matter of fact, no one has ever yet found any evidence to the contrary; though the matter has been studied with more precision than any other problem in the whole range of chemistry. If you had time and facilities for extending your studies to the union of hydrogen with chlorine, and that of hydrogen with nitrogen, you would find the same things true there also. These substances evidently have, so far as can now be seen, an absolutely fixed and invariable composition. These particular cases which we now have under consideration are, moreover, of special interest, because they are substances the component parts of which are, to begin with, *gases*; and as we have seen, there are some peculiarities about gases and their behavior which, when considered in connection with these results of ours, lead us almost irresistibly to some remarkable conclusions.

When we were studying the subject of vaporization we saw that the vapor of any liquid occupies many times the space occupied by the same weight of the substance in the liquid state. This fact, taken together with another which was brought out in the same connection—namely, that several liquids can be successively vaporized into the same enclosed space—strongly suggests that the liquid and vapor alike are made up of *particles* which are separated from each other by distances which must of course be on the average much greater in the gas state than in the liquid state. Since gases like hydrogen, oxygen, and chlorine are nothing but the vapors of very-low-boiling liquids, they must be included under the same head. Another striking fact about gases is, as we have seen, the regularity of their behavior under changes of temperature and pressure. Their behavior is so much alike that it would not be possible to see any difference between the behavior of one gas and another in this respect without pretty careful scrutiny. It is to be expected that small deviations from perfect regularity will appear if the measurements of volume are very carefully carried out; for gases condense to liquids at very different temperatures, and the liquefying-points of some of them are not very far below ordinary temperatures; so it is to be expected that they will show irregularities, unless at very high temperatures, where they are far from their liquefying-points.

In the early part of the present century, two physicists, Amedeo Avogadro, of the University of Turin, and André Marie Ampère, of the École Polytechnique at Paris, arrived independently, and from somewhat different lines of thinking, at what seemed to them to be a possible explanation of the peculiar properties of gaseous matter. It is interesting to note that Avogadro, who published his views in 1811, was mainly interested in the fact that when two gases (hydrogen and oxygen, for example) combine to form a third substance, they always combine in volumes which bear some very simple relation to each other. In the case of water, for example, the ratio is as one to two. Ampère, on the other hand, was particularly interested in the physical behavior of gases when subjected to changes of temperature or pressure. His views on the subject were published in 1814. Both men concluded that there must be some peculiarity of constitution common to all gases. If we consider gases as made up of particles, there must be some regularity either in the nature of the particles or in their number. But if the particle is the representative unit of the gas, and if the properties of any gas (density, color, odor, etc.) are simply the aggregate of the properties of its particles, then it seems improbable that the resemblance will be found in the *nature* of the particles. It is probably, then, a regularity in the *number* of particles contained in a given volume of the gas; and the simplest supposition is that *in equal volumes of any two gases under the same conditions of temperature and pressure there are contained the same number of particles.** This hypothesis explains satisfactorily the facts we have been studying.

If we regard a gas as a collection of material particles endowed with very rapid motion, and at such distances from each other on the average that attractive forces between the particles do not come into action, then the distances between them will be determined by the temperature or pressure conditions to which the gas is subjected. Pressure will act to diminish the average distance between particles, and so will falling temperature. It is easy to see the truth of this statement in the case of pressure; but why rising temperature should act to increase distances between particles is not quite so easily seen without some explanation. In brief, the view on which this rests is that heat is a form of energy; and that heat applied to a gas is in part transformed into energy of motion, which appears in an increased rapidity of motion on the part of its particles. It follows from this way of viewing the subject that if the temperature of a gas be raised, the motion energy of its particles will be increased; and this will result in their being found at greater average distances from each other than before.

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* The terms actually used by Avogadro and Ampère will be considered farther on.

More detailed consideration of this point would be out of place here. We may return to the subject later.

The main point of interest at present is to see what light these two suppositions—namely, that matter in general and gases in particular are composed of particles, and that equal volumes of any two gaseous substances under similar temperature and pressure conditions contain the same number of particles—throw upon the results of our recent studies.

First, let us consider a fact we have established; namely, that a liter of oxygen weighs closely 16 times as much as a liter of hydrogen under the same conditions of temperature and pressure.

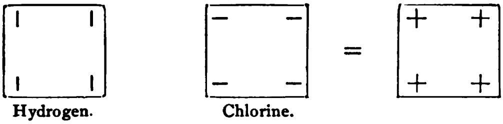
If a liter of hydrogen contains the *same number of particles* as does a liter of oxygen, then this difference in weights must point to a corresponding difference in the weights of the hydrogen and oxygen particles; in other words, the oxygen particle must weigh 16 times as must as the hydrogen particle.

Second. We have seen that hydrogen and oxygen unite in the proportion of two volumes of hydrogen to one of oxygen to form water. Now since two volumes of hydrogen contain twice as many particles as one volume of oxygen, it follows, if the acts of a gas are the acts of its individual particles, that in order to form the water particle twice as many hydrogen as oxygen particles are needed. Or in other words, the water particle contains twice as many hydrogen as oxygen particles. What the precise numbers may be we cannot yet say.

Finally comes the fact that when two volumes of hydrogen and one of oxygen unite, we obtain two volumes of gaseous water. We may well consider in connection with this case that of hydrogen and chlorine, which, as we have seen, unite in equal volumes to form two volumes of the resulting gaseous product. In fact, since the numbers in this latter case are a little simpler, we may find it convenient to consider it first.

In the first place, let us see if we can get any information as to the probable complexity of the particle which is formed when hydrogen and chlorine particles unite. Is it composed of one particle of hydrogen and one particle of chlorine? Or is it made up of two or of three particles of hydrogen and an equal number of particles of chlorine?

If we represent the volumes of hydrogen and chlorine by equivalent squares, as below; and if we represent the number of particles by convenient signs, we can perhaps picture the matter more clearly to our minds. Let us deal with such a volume as contains, say, *four* particles of any gas. Now if one particle of hydrogen and one particle of chlorine unite to form one particle of the product, we should have the result represented below.



That is, according to our present notions of particles, one volume of gas product ought to result. *But as a matter of fact two volumes of gas product are formed.* The most obvious conclusion to be drawn would seem to be that the new particle contains half a particle of hydrogen and half a particle of chlorine.

We may approach the subject in a slightly different manner. The volume diagram we have just considered shows one thing certainly: that the particle of the gaseous product in this case cannot contain *more* than one particle of hydrogen and one particle of chlorine. Let us assume, then, for a moment, that this is the composition, and see what follows. In order to keep clearly in mind the conditions, let us once more represent the action by squares, each of which we will now suppose to contain four particles. We should then express our results of actual experiment as follows:

$$\boxed{\begin{array}{c}4\\ \text{Hydrogen}\\ \text{particles.}\end{array}} + \boxed{\begin{array}{c}4\\ \text{Chlorine}\\ \text{particles.}\end{array}} = \boxed{\begin{array}{c|c}4 & 4\\ \text{new} & \text{new}\\ \text{particles.} & \text{particles.}\end{array}}$$

Now if each new particle contains one particle of hydrogen and one of chlorine, each of the eight new particles must contain a hydrogen particle; and, by the same reasoning, must also contain a chlorine particle. Hence, adding up the particles we started with, and comparing the sum with what we obtained at the close, we should have

$$\begin{array}{c}4 \text{ hydrogen}\\ \text{particles}\end{array} + \begin{array}{c}4 \text{ chlorine}\\ \text{particles}\end{array} = \begin{array}{c}8 \text{ hydrogen}\\ \text{particles}\end{array} + \begin{array}{c}8 \text{ chlorine}\\ \text{particles}\end{array}.$$

That is, *we turn up at the end with twice as many particles as we started with.*

This result evidently leads to the same conclusionwe reached by our former reasoning. Both agree that *the hydrogen and chlorine particles are apparently halved in this process.* There is, in fact, no possible escape from the conclusion; and on the basis of numerous similar cases, supplemented by strong independent evidence from other sources, chemists believe to-day that the hydrogen particle, as it exists in ordinary free hydrogen gas, is actually *double;* that is, consists of two smaller particles; and that the same is true of chlorine.

If now we examine our water results by a similar line of reasoning, we shall arrive at a similar conclusion in regard to oxygen. For we have:

$$\begin{array}{c}\boxed{\begin{array}{c}4\\ \text{Hydrogen.}\end{array}}\\ \boxed{\begin{array}{c}4\\ \text{Hydrogen.}\end{array}}\end{array} + \boxed{\begin{array}{c}4\\ \text{Oxygen.}\end{array}} = \boxed{\begin{array}{c|c}4 & 4\\ \text{Water.} & \text{Water.}\end{array}}$$

If the particle of water contained simply two particles of hydrogen and one of oxygen, we should get only *one volume of water* (gaseous). As a matter of fact we get *two volumes;* so it appears that the water particle must contain two hydrogen *half-particles* and one oxygen *half-particle.* We could arrive at the same result by counting up the particles used, and the resulting particles, as we did in the preceding case.

Further, nitrogen and hydrogen, as we have seen, exist in ammonia-gas in the proportion of one volume nitrogen and three volumes hydrogen.

If this case be studied out along similar lines, it will be seen that the nitrogen particle, too, must be double.

Throughout this discussion, one matter has been troublesome; we have had occasion to use the word "particle" to mean at least two different things. Now, however, since we have recognized the existence of two distinct kinds of particles, we may well adopt the names which chemists have given to them.

First, then, we call these little half-particles *atoms.* All particles that consist of two or more 'atoms,' whether these atoms are like or unlike, we call *molecules.*

Even on the basis of our work thus far we can distinguish two classes of molecules. A good example of the first class is the hydrogen molecule with its two atoms *of the same kind.* Such molecules we call *elementary molecules;* and the substance which results from the aggregation of immense numbers of such molecules we call an *element.* The word 'element' means, then, simply that so far as we know the substance is composed of only one kind of matter; or, in other words, that its molecule contains only one kind of atom.

A good example of the second kind of molecule is found in water or in hydrogen chloride, which is the substance formed by the union of hydrogen and chlorine. In both these cases the molecule is composed of atoms *of different kinds.* Such molecules are called *compound molecules;* and the substances they represent are called *compounds*. We see, then, that the word 'compound,' which is in some respects an unfortunate term, has for the chemist a very clear and specific meaning, very different from the sense in which the word is commonly used. No substance can be called a compound until it can be shown by conclusive experiment:

1. That the substance is perfectly homogeneous;
2. That it is made up of molecules of definite and invariable composition; these molecules always containing the same kind and number of atoms, whatever the method of preparation.

In case of water, for example, this proof is complete and convincing; and a careful review of our studies on this subject, from the time we first burned hydrogen in the air, cannot fail to result in clear ideas as to what is meant by a *chemical compound*.

In conclusion, let us consider for a moment this word *atom*. It is a term that dates back to the days when all was speculation, and it was used, as its derivation shows, to designate a portion of matter that could not be further divided. As used to-day, the word carries with it much the same idea; but the chemist thinks of the atom as indivisible, not on account of anything necessarily connected with its *size*. It is indivisible in the same sense that a man is indivisible, and only in that sense. The atoms bear the same relation to the processes we call chemical as we do to the operations which are carried out through the agency of the human race. They are the individuals, the people of our chemical world. The idea of the atom is, then, a perfectly rational and sensible one, the joint production of sound experimental fact on the one hand, and common sense on the other.

LABORATORY WORK.

Determine the percentage composition of cupric oxide. This can be easily done by weighing out, in the same hard glass tube as was used in determining the composition of water by weight, cupric oxide (powdered) enough to fill it between the asbestos plugs; taking care to leave a channel between the top of the tube and the oxide, so that there will be no danger of the tube's becoming plugged. The oxide had better be heated in the iron crucible, to expel moisture, and then cooled before weighing out. The tube also should be carefully dried out. Weigh first the tube, then the tube + the cupric oxide.

Connect the hydrogen generator, as in the former experiment, and sweep out all air (test). Then heat the tube from end to end as before till no more water is formed. Cool thoroughly in the current of hydrogen; then detach the generator, allow the tube to stand in the air for ten or fifteen minutes open, so that the hydrogen inside may be replaced by air, and then weigh. The loss of weight of tube and contents is the oxygen. By subtracting this from the total weight of cupric oxide taken we get the copper. Calculate the per cent of copper and oxygen.

LECTURE 21.

OUR recent studies have had the effect of bringing forward prominently the following ideas, which must be kept clearly in mind from now on:

1. The idea of the *molecule*. To the chemist the molecule is interesting not in and of itself as a unit, but on account of its being *composite*, or made up of atoms, and capable of decomposition with formation of new molecules. The physicist, on the other hand, considers the molecule simply as a mass of matter—in the same way that the astronomer treats the earth—without considering its inner structure.

2. The idea of the *atom*—the individual of the chemical world, very small but still finite; unchangeable as to mass and properties, so long as the present universe endures.

Since molecules and atoms are finite things, the question as to their weights is evidently a perfectly legitimate one. And since we can gasify many forms of matter, it is clear that if we continue to accept the guidance of Avogadro's hypothesis, we can determine how many times heavier one molecule is than another, simply by comparing the weights of equal volumes of the substances under investigation, in the gaseous state, and under the same temperature and pressure conditions.

If, now, we could find some molecule which was lighter than any other, we could use that molecule as a standard, and express the weight of any other molecule by saying how many times heavier it was than the standard molecule. In searching for such a standard, we find it in the hydrogen molecule, which is at present the lightest known. The only difficulty is that if we use the hydrogen *molecule*, the weight of the hydrogen atom referred to it will be ½. This is rather awkward; so as a mere matter of convenience chemists have decided to take the *hydrogen atom* as the standard by which all other atoms and all molecules shall be weighed. The weight of any molecule referred to *the hydrogen atom* is called its *molecular weight.* Note carefully that the adjective *molecular*, as used here, simply calls attention to the fact that *we are weighing a molecule*, and does not at all refer to the standard. Similarly, the weight of any atom, in terms of the hydrogen atom, is called its *atomic weight:* and note here also that the adjective *atomic* serves to remind us that what we are considering is *an atom* and not a molecule. It is obviously improper to speak of the atomic weight of a compound; for its smallest representative particle is a molecule and not an atom. On the other hand, an element, whose molecule contains more than one atom (like oxygen, for example) has both an atomic weight and a molecular weight.

The molecule of oxygen consists, as we have seen, of two atoms; therefore the molecular weight of oxygen is twice its atomic weight, the numbers being 32 and 16 respectively.

As a good example of a molecular weight determination, let us consider the case of water. We first must obtain a comparison between the weight of one liter of gaseous water at some convenient temperature and pressure, and the weight of one liter of hydrogen under the same conditions.

To do this a glass flask or globe must be filled with steam at a temperature sufficiently above 100° and at atmospheric pressure. This is generally accomplished by introducing some water into a flask provided with a rather slender neck which can be drawn down, in the blowpipe flame, to a very fine opening. The flask with its contents is placed in a bath heated to, say, 150° until steam no longer escapes from the capillary outlet. When this point is reached, it is clear that the interior of the globe is filled with steam at 150° and at atmospheric pressure, and the globe is then sealed by the blowpipe flame as quickly as possible. The weight of the flask and steam is now determined with all possible care, and the flask is then opened, cleaned, and dried; and the weight of the flask alone determined. Finally its internal volume is measured.

We will assume the flask to have held one liter of steam at the observed temperature and barometric pressure. The barometric pressure we will take as 760 mm.

As a result of such experiments it appears that one liter of steam at 150° and 760 mm. weighs 0.5216 grams. At the same temperature and pressure one liter of hydrogen weighs closely 0.0579 grams.

In order to compare these weights, we divide the weight of one liter of steam by the corresponding weight of a liter of hydrogen, and obtain $\frac{0.5216}{0.0579} = 9.$ very closely. Therefore the molecule of water is 9 times as heavy as the *molecule* of hydrogen; but we wish to compare the water molecule with the hydrogen *atom*, which is half as heavy as the molecule: It is clear that the weight of the water molecule referred to this standard will be 18; which is, then, the *molecular weight* of water.* Any substance which can be converted into a gas at a manageable temperature, and without undergoing decomposition, can be treated in the same way.

One point needs to be clearly understood. The method is at best an approximation, more or less close according to circumstances. For example, it is more accurate in case of substances which are gases at ordinary temperatures, than in case of such a substance as water, which is a liquid at ordinary temperatures; because in the former case what is sealed up in the bulb is more truly gaseous than in the latter case, when the temperature at the time of sealing the globe is not very much above the boiling-point. It follows that in applying this method it is desirable to have the temperature at which the liquid is gasified as high as is possible without increasing too greatly the difficulties of manipulation.

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* See *The New Chemistry*, p. 79; also Richardson, p. 59, where a simple lecture-table experiment on this point is described. More extended descriptions can be found in any large work on physics or chemistry.

In ordinary cases, however, the method is accurate enough to enable us to decide whether the molecular weight of a substance is a certain number or some multiple of that number, which is the form in which the question ordinarily comes up. For example, the value experimentally determined for the molecular weight of water, when considered in connection with our studies on the composition of water by weight and volume, proves that the molecule contains two atoms of hydrogen and one of oxygen.

LECTURE 22.

We have now studied in considerable detail some of the ideas and methods which are fundamental in every physical science. We have, moreover, gained some idea as to the nature of the changes in matter designated as *chemical changes*. We are now ready to extend our study to elements other than hydrogen and oxygen, and to compounds other than water. At the very outset of this study, it must be kept clearly in mind that every truly chemical process is at present regarded as taking place between molecules and atoms, molecules and molecules, or atoms and atoms, and this idea is in accord with everything we have at hand in the way of facts. But it must also be remembered that we never see any of these actions in their simplest form. For example, no one has seen, or ever will see, two hydrogen atoms and one oxygen atom unite to form the water molecule; and we do not at present know what sort of an action it would be if we could see it. What we actually do see is the union of two volumes of hydrogen and one of oxygen to form two volumes of water-vapor. When we see sulphur, phosphorus, zinc, magnesium, or any other substance burn in the air, we feel sure, after careful study, that what is actually taking place is a union between oxygen atoms and atoms of sulphur, phosphorus, or magnesium; and no matter how complex the burning substance may be, we still believe that the only thing that is going on is the union of oxygen atoms with the atoms of one or more of the constituents of the substance.

All we actually see, however, is a lump of the substance burning in the air, and gradually disappearing. Since this is so, it will evidently be wise to study such actions from a point of view which will take things as we actually find them.

In order to make this point clear, let us study for a while the action of oxygen upon different substances, the conditions under which it takes place, and the causes which modify it.

According to our present light, it would seem likely that there is some kind of attractive force which brings atoms together and holds them together as a molecule. Judging from what we see of its operations, this attractive force differs from other such forces, such as gravitation and magnetism, in that it seems to act only at exceedingly small distances. It follows, then, that in such an action as the burning of a substance in air or oxygen, the rapidity of the burning, that is, *the quantity burnt in a given time*, will depend largely upon the amount of surface which the substance offers to the oxygen; because it is only where the substance and oxygen come in contact that the action can take place. When we cut into a partially burnt log or stick of wood, we find the interior for the most part unburnt and unaffected. The burning is all on the outer surface. It would seem, then, that if we could by any means increase the surface exposed, we should get a more rapid burning. One way we can always take is to reduce the substance to fine powder or dust; and the effect is very remarkable in some cases.

For example, if we lay a small dry piece of ordinary phosphorus on a piece of asbestos paper, it may take fire before the end of the lecture, and it may not.

Now let us reduce some phosphorus to a very fine state of division. For this purpose we will dissolve a little piece in bisulphide of carbon and pour out some of the solution on a piece of filter-paper. As the volatile bisulphide of carbon evaporates, it leaves the phosphorus behind spread over the fibers of the filter-paper. By this means a very little phosphorus is spread out over a considerable amount of surface, and very soon after it has dried, the phosphorus on the paper takes fire and burns.

In the second place, let us consider the burning of a much more common substance,—iron. The burning of iron is certainly not a very easy matter when we have the metal in moderate-sized lumps. Here, however, is some iron in very fine powder. We pour out a little heap of it on a piece of asbestos paper, and touch a lighted match to it; and you see how the whole heap glows. As we stir the iron powder so as to get new surfaces exposed the burning continues. Here is some more powdered iron, which was made from finely powdered *oxide of iron*, which is one of the compounds that iron forms with oxygen. This fine powder was placed in a glass tube and heated gently in a current of hydrogen, just as we once heated the oxide of copper. Water was formed; and very finely powdered metallic iron was left behind. This finely powdered iron was allowed to cool in the current of hydrogen; and the tube was then sealed up. Now on opening it, and pouring the iron out in a heap on the asbestos paper, it glows and burns *even at the ordinary temperature*, just as the phosphorus did. Finally, here is a tube in which there is some very finely powdered metallic lead, which was prepared by a process somewhat like that just described.* When the metal is poured out, you see it takes fire and glows just as the iron did.

In all these cases, then, we see there is, just as might be predicted, a marked increase in the rapidity with which "oxidation" takes place, as we increase the amount of surface exposed. This fact has one or two important practical bearings. In the first place some of the substances we call *oils* oxidize on exposure to the air. The oils are rather complex in constitution, and the products of the oxidation are naturally more complex than in the cases we have just been considering; but the process is essentially the same in all cases. Linseed-oil, which is so commonly used in mixing paints, oxidizes readily on exposure to the air, and the product is a resinous substance. The result is that when linseed-oil stands for a few hours exposed to the air, it becomes covered with a thin "skin" of this resin; hence the "paint-skins" so frequently seen in paint-pots. Many other animal and vegetable oils act similarly, and such as do are called *drying-oils*, since the product is generally a resin, and the oil appears to dry and become resinous. It is from this cause that the so-called "oil-colors" dry and become hard. Now whenever a substance oxidizes there is always some development of heat; and when an oil oxidizes, in the manner just described, it rises in temperature. Of course if it is simply standing in a pail or on the wall of a house exposed to constant circulating currents of air there will be no perceptible temperature-change; but if it is spread out over the fibers of a cloth in a space where there is little air, and that not in circulation, the temperature may rise high enough so that the cloth will take fire; or, in other words, the oxidation will become so rapid and intense as to be attended with light and heat.

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* Heat dried tartrate of lead in a test-tube, the open end of which has been drawn out to a fine jet. When no more vapors are evolved seal the jet.

Many of the lubricating-oils used around engines and other machinery show this behavior, and it is, accordingly, a rather dangerous proceeding to put pieces of cotton waste, or old rags saturated with oil, away in places where there is no air circulating. Soft coal contains some substances which oxidize readily, particularly in moist air. A heap of soft-coal "screenings," if examined several hours after it is put into the bin, will be found to be decidedly warm in the portions nearest the bottom of the heap; and sometimes the temperature rises sufficiently to set the whole heap burning. This takes place on shipboard sometimes when coal is the cargo.

The screening-piles in the vicinity of soft-coal mines are always burning round the base, and they take fire from the cause above described.

Another circumstance which may decidedly modify the practical results of the action of oxygen (or anything else, in fact) upon a substance is the *physical state and nature of the product.*

If, for example, the substance acted upon be a solid substance, and the product also a solid, not perceptibly volatile at ordinary temperatures, then when the surface has oxidized, and thus formed a coating of the product, this acts as a protection to the interior portions, which can only be attacked by such oxygen as works through the outer coating; and this action must necessarily be slower than when there is easy access of oxygen. This fact is of very great practical importance. For instance, the so-called Russia iron, used in making stovepipes and in covering locomotive boilers, is merely sheet iron coated artificially with a thin layer of oxide of iron. Bronze statues which are to stand out of doors exposed to the weather are previously exposed to moist air under carefully regulated conditions, or washed with certain solutions, so that the green substance which forms on the surface of copper, brass, or bronze on exposure, may form in a very thin uniform layer, instead of forming in irregular patches as it might if left to the weather. A "paint-skin" serves the same purpose. It forms a thin layer of material upon which the oxygen of the air has done its work, and which protects the remainder of the paint or oil, as the case may be. Aluminum, the metal which has recently come into such extensive use, oxidizes on exposure, particularly in moist air, but the product formed is a solid, and insoluble in water. The result is that only a very thin layer forms on the surface, and this protects the rest. Moreover, since the oxide happens to be *white* and since the coating is very thin, it is not much of a disfigurement. The statement has often been made in print that aluminum does not corrode; but the statement is not an accurate one, though it is true that the metal does not lose its color and luster so markedly as some other of the common metals.

From these studies on oxidation it is clear that we must expect to find that in other kinds of chemical action the physical condition of both reacting substances and products will play, to say the least, an exceedingly important part.

So true is this, and so largely does the course of a chemical reaction depend upon these circumstances, that we shall find it much to our advantage to give very careful thought and study to them, before undertaking to explain them by any appeal to "affinities" of different strengths.

LABORATORY WORK.

As a first step in the study of other chemical actions we will study, in some detail, the products formed on burning certain elementary substances in air or oxygen. The burning is carried out in a quick-sealing fruit-jar under conditions described below. The substances to be burned are sodium, magnesium, zinc (dust), sulphur, phosphorus, carbon (charcoal powder). Some form of iron spoon will be needed. The best form has a circular bowl about an inch across. The handle is at right angles to the bowl, and is provided at the top with a cross-piece which rests on the rim of the jar. If such a spoon be employed, the first step is to place in the bowl a small quantity (a gram or so) of the substance to be burned. Heat over the burner till the material begins to burn; then bring the spoon into the jar (which should contain a few cubic centimeters of water), and put on the lid. When the burning is over, examine the jar, and try to determine whether the product is solid, liquid, or gaseous. If any of the product sticks to the spoon, scrape it off into the water. Finally shake the jar with its contents, so as to bring the product of the burning thoroughly in contact with the water in the jar. Ascertain whether any of the product has dissolved. (How can you do this?) If it has, then see whether the solution has any effect upon paper colored with litmus solution. Some of the paper will be blue, and some red. Try both kinds. In trying this test, dip a glass rod into the solution so as to take out a single drop, then touch this to the small strip of paper. Take care to use a fresh dry place on the paper each time, and be sure that you are familiar with the appearance of both kinds of paper when simply moistened with pure water.

Do any of the *unburned* substances dissolve in water at all? Try each substance separately. Is there, in any case, perceptible action, or effect upon the paper?

In order to study out in detail the action of sodium upon water, several pieces of the metal, about the size of a small pea, will be needed. Then the following line of study can be pursued.

Compare the solutions obtained (1) by burning sodium in oxygen (or in air), and dissolving the product in water; (2) by simply bringing sodium in contact with water.

Evaporate the two solutions, and compare the residues (all this work should, of course, be carefully and completely recorded). Does contact with the air have anything to do with the second case? Can you devise an experiment to test this point? Your experiments as planned should be in *practical form*, and should, as a rule, involve only apparatus actually in your possession. Does solution (2) contain sodium or not? Sum up such circumstantial evidence as indicates that it does, and such as indicates that it does not. Which is the stronger case?

From your comparison of the two solutions (see above) does it seem probable that the substance obtained by the action of sodium upon water contains oxygen? Bring together and arrange all the evidence you can muster bearing upon this point. What does it indicate?

If there is oxygen in the substance, whence does it come (that is, when the substance is made by the action of sodium upon water)? Evidence? Fill a test-tube with water: close it with the thumb; invert it in a pneumatic trough, or in an evaporating-dish containing water. Fix a small piece of sodium upon the end of a file or a piece of wire, and plunge it *quickly* under the rim of the inverted test-tube, which should be *very* near the surface of the water, so that the metal may rise through the water to the top of the water in the test-tube. What is the result as seen? How do you interpret it? Does it throw any light upon the investigation in which you are engaged?

Does it now seem probable that the substance contains hydrogen? Is the evidence satisfactory either way?

A. Take a little of the solution made by acting upon water with sodium. (It will be well to furnish the student with a rather stronger solution than the one he has at hand.) Take a piece of metallic aluminum (an element) and put it in the solution. What happens? Now try the action of aluminum upon plain water. Does this experiment seem to you to throw any light upon the question in hand? In what respect is it inconclusive? Is the following one better?

B.* Take a piece of hard glass tubing about ¼ of an inch inside diameter and 2⅛ inches long. Seal one end (taking care not to make too thick an end). There will be furnished you a piece of the substance you are studying, about the size of a large pea. Put this in your tube. Fit a small cork to the open end and attach a short delivery-tube (or else make a rubber sleeve-joint). Now remove the cork; clamp the little tube in an inclined position, and heat it gently and carefully over the Bunsen flame until the substance *just melts quietly without any bubbling. Cool.* Put in a piece of clean, bright magnesium ribbon about an inch long; replace the cork, and heat again in the lamp a little hotter than before. See if you can gain any evidence that hydrogen is given off. The gas given off can be collected over water. *Be careful not to stop heating the tube for an instant so long as the delivery-tube is under water.* When you are ready to stop heating, the delivery-tube should be lifted out of the water, and the cork removed before the lamp is taken away.

Whence must the hydrogen come, if magnesium is an element? How do you know it does not come from water in this case?

So far as can now be seen, what seems to be the constitution of the substance obtained by acting upon water with sodium, or by burning sodium, and dissolving the residue in water?

Weigh a small beaker containing a few c.c. of kerosene. Put in enough sodium in small pieces to make about 0.2 gram. Ascertain the exact weight of sodium in the beaker. Now put into a weighed evaporating-dish about 25 c.c. of water. Remove successively the little pieces of sodium from the kerosene; wipe each one with filter-paper, and put it into the water (let each piece disappear before you add another). When all has been added, carefully evaporate the contents of the dish to dryness, taking care not to spatter, and heating gently near the close of the evaporation. *Just melt* the residue in the dish; allow the dish to cool until the hand can be borne upon it; then dip the bottom of the dish into cold water to cool it quickly; wipe clean and dry and weigh again, carefully recording the weight. Does the substance weigh more than the original sodium? Does this experiment add anything to your previous results?

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* This can be made a lecture-table experiment if the class is very large, but it is not a difficult piece of work at all and requires only average caution.

We now know how much of this sodium compound we are studying can be obtained from a given weight of sodium. The two other facts we have observed are that hydrogen is evolved when sodium comes in contact with water, and that the resulting compound, when freed from water by evaporating the solution and melting the residue, will yield more hydrogen when heated with metallic magnesium. (Metallic sodium could be used here: magnesium works rather more smoothly.) Now suppose we should take a known weight of sodium, bring it in contact with water and measure the hydrogen evolved; then evaporate the solution, heat the residue with metallic magnesium, and measure the hydrogen evolved; would there be any relation between the volumes of hydrogen collected in the two cases? We cannot conveniently try the experiment in this form, but we can easily get at the result by a little variation of the process. First we need to know what volume of hydrogen is evolved when a known weight of sodium comes in contact with water. Take a piece of lead pipe about 2½ cm. long and 4 mm. bore. Close one end by hammering the edges firmly together. Weigh it; then pack it *solidly* with metallic sodium. (The metal must be in one piece and must be forced *very tightly* into place.) Weigh again, and the increase is the sodium taken. Fill a flask or jar with water; invert it in the pneumatic trough; and bring the little sodium tube under it. When all the hydrogen has come off, measure its volume and record it. Now calculate from the results of your last experiment (see p. 120) how much of the compound must have been formed by the action of the quantity of sodium you have just used upon water. If now we can take exactly this weight of the dry compound *already prepared* and heat it with magnesium, we shall do what is equivalent to evaporating the solution just made, and using the residue.

Take another short piece of hard glass tubing closed at one end, just like the one used on p. 120. Counterpoise it, then put in enough small pieces of the solid sodium compound (which will be furnished) to make about 0.2 gram. Ascertain the exact weight you have taken. What volume of hydrogen would have been formed in making this amount of the compound? Calculate and record it. Roll about 8 centimeters of magnesium ribbon* into a tight bundle about 1½ centimeters long. Heat the little tube containing the sodium compound till the substance melts. Heat the entire tube gently so as to drive off all water, then cool, drop in the magnesium, adapt the delivery-tube, arrange a flask or jar to collect the gas; and heat the mixture, at first gently, afterwards to dull redness, until no more gas comes off even on pretty strong heating. *Remove the delivery-tube from the water.* Stop heating, and detach the delivery-tube. Measure the gas collected. Compare its volume with the volume that would have been evolved in making the quantity of sodium compound you used. How do they compare? Remembering the constitution of the water molecule, do your results give you any possible clue to what happens when the sodium atom acts upon the water molecule?

Let us now study the substance obtained by oxidizing phosphorus and dissolving the residue in water.

It is clear that the product of the simple burning contains oxygen. Does it necessarily follow that the oxygen is still in the substance after it has been dissolved by water? If it could be shown that the product of the burning *lost nothing* by solution in water, and *gained something*, would that in your judgment be sufficient evidence to make it probable that the substance formed when phosphorus is burned in the air, and the product dissolved in water, contains oxygen? Experiment as follows:

Arrange two clean *dry* fruit-jars mouth to mouth as shown in the sketch (see Fig. 35). The joint between the two jars can be made tight enough by putting in a "packing-ring" of asbestos paper or cloth as shown. Place in the bottom of the upright jar a porcelain crucible or any other convenient little dish, containing two or three grams of *red* phosphorus. Drop a red-hot bead of glass upon the phosphorus to light it. Place the upper jar in position as shown in the figure. When the burning slackens lift the upper jar an instant to let in more air. The whole of the phosphorus can thus be burned in a few minutes, and we obtain a satisfactory quantity of the product. When the phosphorus is all burned, allow the jars to stand for a minute, until most of the white product has settled; then dismount the jars and rapidly scrape out the white snow-like solid onto a sheet of paper. Transfer it *at once* to a *dry* test-tube. Cork the tube and ascertain the weight of test-tube, cork, and contents.

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* Recent experience shows that rough iron turnings give the best results here.

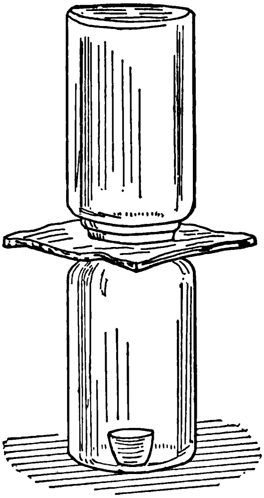

FIG. 35.

Next prepare and weigh an evaporating-dish containing about 10 c.c. water. Shake the white powder into the water with stirring, rinsing the tube if any sticks to the sides. Set the solution evaporating over a moderate flame. Meanwhile clean and dry the test-tube and weigh it with its cork. This weight subtracted from the original one will give the weight of the white product experimented upon. Returning now to the solution, heat it gently until no more water goes off, and there is left a sirupy residue. This is the substance you are after. Cool the dish * and reweigh. Subtract the weight of the dish. The difference is the weight of your final product. Compare it with the weight of the white product obtained by the union of phosphorus with the oxygen of the air. Is there any *marked* gain in weight? Does the result assist you in arriving at a conclusion?

Considering now that the sodium compound produced by processes similar to those we have been through, contained hydrogen, does it seem probable that the substance now under consideration contains hydrogen? Try the same experiment as before; i.e., take the little hard glass tube with cork and delivery tube, and heat some of the sirupy substance with magnesium. Do you obtain any hydrogen?

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* Dishes should *never* be weighed unless they feel *cool* to the touch. If weighed warm, the weight will always be low, for the warm air rising from the pan containing the object, gives rise to an ascending current of cold air from below, and this air-current tends to lift the pan.

So far as can now be seen, what seems to be the constitution of this substance?

LECTURE 23.

OUR studies as to the action of various oxides upon water have brought to light two different modes of behavior. It is true that some oxides show no visible effect either way, but in all such cases it has been found that the oxide would not dissolve in water; or, at least, that the quantity taken into solution was too small to affect the litmus paper. The oxide of zinc is a case in point. On the other hand, such oxides as that of sodium, which dissolve readily in water, always show a decided reaction one way or the other. It may be interesting to see an intermediate case, where the oxide is somewhat soluble, but not very. Here is some oxide of calcium. The element calcium is very difficult to prepare. Fortunately, however, its oxide is a commercial article, and plenty of it is available. It is called *lime;* and is commercially prepared by heating limestone or marble to a white heat. If now we take a weighed lump of the substance, and moisten it with water, it begins after a few minutes to steam and crumble, and finally falls away to a *dry* white powder; which, however, weighs considerably more than the original lime, as can be ascertained by reweighing it.

Placing some of this white powder in water and shaking, you see the solution is milky, showing that not all the substance is dissolved; but on filtering a little of it, and trying the litmus test, we can easily see that some has dissolved, for the paper turns decidedly blue.

In the second place, we have succeeded in arriving at some conclusions as to the constitution of the substances contained in these solutions. We have examined one representative of each class, and in both cases the substance seems to contain, besides the element burned, hydrogen and oxygen. If we should extend our study to the rest of the known elements, we should find nothing new in this line. Some would show no effect at all, for reasons just mentioned; but where there was any effect, it would be either a reddening or bluing of the paper.

We can then if we choose divide the elements into two classes, on the basis of the behavior of their oxides toward water; and if we should sort them in this way, we should soon see other reasons for believing that the behavior of the oxides is only one among many signs that we are dealing with a genuine difference.

In order that you may see some of the most obvious of these relations, here are the elements you have actually burned, and some others.* The eye at once perceives certain differences between these two groups. Any one would describe one group as *metallic*-appearing substances. It is very hard to express, in any other words, the idea conveyed by this word *metallic*. Every one understands what is meant when a substance is said to have a metallic appearance, for the word carries its own meaning. One idea it conveys to us is that of a peculiar lustre which the polished surface of such a substance possesses; and which is called *metallic lustre*, to distinguish it from the lustre of such substances as glass, which is called *vitreous lustre*. On closer study, we should find that these metallic-appearing substances are heavier than the others, as a rule, and that they are good conductors of heat and electricity. In fact, as soon as our eyes were once opened to the very evident difference in the physical properties of these elements we have been studying, we could classify, at once, many other elements which we could not classify on the basis of the behavior of their oxides toward water. On any basis, however, this classification of the elements into *metals* and *non-metals* is not an absolutely sharp one; and some elements seem to belong to both classes. Nevertheless there are two kinds of characteristic behavior; and toward one or the other of these, every element inclines more or less decidedly.

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* Sodium, magnesium, zinc, iron, lead, copper, aluminum, **mercury**, sulphur, phosphorus, carbon, bromine, iodine.

The difference between the compounds which the metals and the non-metals form with hydrogen and oxygen is especially noteworthy.

The oxides of the *non-metallic* elements, when they dissolve in water at all, give solutions which turn litmus red. The substance in solution which causes this action, and which consists of the non-metal united with oxygen and hydrogen, is called an *acid.* We shall see later that some acids do not contain oxygen, but all of them contain hydrogen. The substances of the other class which turn litmus blue are called *bases.*

The next matter to be studied is the action of acids upon bases. For this purpose we will take one of the most common acids—hydrochloric acid, which is simply a solution of hydrogen chloride gas in water,—and act upon it with the alkaline substance which we obtained by the combined action of air and water upon sodium; and which is called, quite appropriately, *sodic hydroxide.*

LABORATORY WORK.

Begin your experiments by measuring out in an evaporating-dish about 10 c.c. of a solution of sodium hydroxide. The solution should be filtered if necessary. Next secure about half a test-tubeful of dilute hydrochloric acid (about 1 acid to 4 water) and two small strips of litmus paper, one blue, the other red. Add the acid to the alkaline solution in small portions at a time, stirring constantly and testing frequently. In order to test, the glass rod should be dipped into the solution and touched to one edge of the litmus strip. A very small spot is sufficient to show the color. The litmus paper should *never* be put into the solution. If the work be carefully done, a point will finally be reached at which the solution affects neither paper at all. Now there are two ways of regarding this result. It may be that the acid and base are both there still unchanged, and that the neutrality is simply due to the fact that they are present in such quantities that each balances the effect of the other—or it may be that they have actually reacted with each other to form a new substance whose water solution is neither acid nor alkaline. In order to test this point make the following experiments.

1. Take some of the original acid in the evaporating-dish and boil it to dryness. There is no need to evaporate the sodium hydroxide solution, for you know the properties of the residue it will yield. Finally evaporate the neutral solution, and compare the residue with those obtained by evaporating the acid and alkaline solutions. *Note and record fully the respects in which they differ.*

2. Take 10 c.c. more of the sodium hydroxide solution; and measure out in a test-tube about the amount of acid needed to neutralize it. Take their temperatures. Now pour them rapidly together; stir, and take the temperature again.

You have no reason to assume that in *every* case where substances actually react there will be a rise of temperature; but in most of the cases you have thus far seen there has been such an effect; and the observation has therefore a certain amount of significance. Which seems to you now the more reasonable view as to this neutralization process?

Let us now see if we can get some idea as to the constitution of the substance contained in the neutral solution. The first question is: how many distinct substances can we distinguish in the solution? Certainly one substance, perhaps more, is to be found in the residue left upon evaporation; and we may find others in what boils off. At all events it is necessary to try.

Arrange an apparatus as shown in Fig. 36. The small flask has a capacity of about 50 c.c., and the delivery-tube runs through the perforation of a notched cork into a test-tube which is kept immersed in cold water nearly to the cork. Neutralize about

10 c.c. of the sodium hydroxide solution; and pour the neutral solution into the flask. Clamp the flask in position, and boil the contents by means of a low Bunsen flame. Toward the last, the heating must be carefully managed or the flask will be broken. At no time should the Bunsen lamp be out of the hand; and care should be taken that the flame does not heat the portions of the flask not touched by liquid. Evaporate until practically all liquid has distilled over into the test-tube. Examine this liquid; note its color, taste, odor, reaction with litmus, and its boiling-point. What does the liquid appear to be?

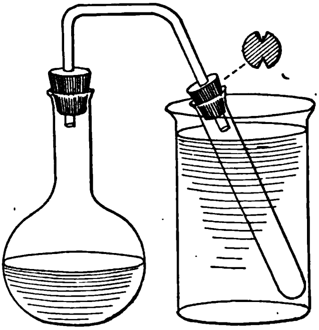

FIG. 36.

Dissolve the residue in the flask in the smallest possible amount of water. Filter the solution, and place it in a flat "crystallizing-dish." Allow it to stand for some hours and then examine carefully the crystals that separate from the solution. Does the substance appear to be uniform (homogeneous) throughout, or do there appear to be several different forms of crystals?

In order to see whether other acids will give results of the same nature, take about the same quantity as before of sodium hydroxide and neutralize it with nitric acid. Examine this case as carefully as you did the previous one. Are the results like those obtained in the first case or not? Make a third experiment, using this time potassium hydroxide and sulphuric acid: thus varying both acid and base. What results do you obtain?

In what respect do these three reactions differ?

In what respect are they alike?

Finally, what is the nature of the substance which appears when the neutralized solution is evaporated?

Let us first consider the particular product obtained when sodium hydroxide and hydrochloric acid are brought together. The question is: putting together the facts you have accumulated, what seems to be the most reasonable conclusion as to the constitution of the white substance left on evaporating the neutral solution? Bring together and arrange all the facts and observations you have that in any way bear upon this point. What kind of evidence is needed, in your judgment, to confirm your conclusion? Think the matter over carefully before you go onto the next.

Take a small beaker (see Fig. 37). Cut a round piece of asbestos paper to fit the bottom (inside). Cut another piece to fit over the top for a lid. This piece should have a small hole in it to allow the introduction of a slender glass tube.

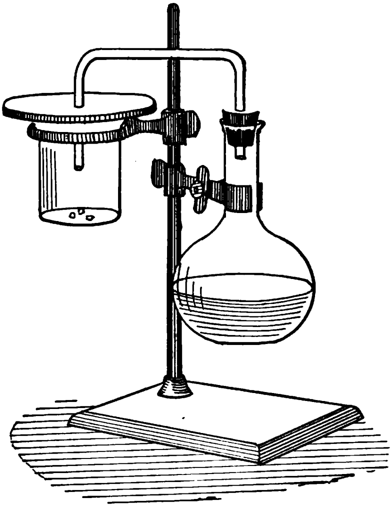

FIG. 37.

Take a 50 c.c. flask, and place in it a few small lumps of manganese dioxide, and just enough strong hydrochloric acid to cover the lumps. When this mixture is warmed gently it gives *chlorine*. Now fit the little flask with cork and delivery-tube as shown in the figure, and clamp the flask in position, with the delivery-tube passing through the hole in the asbestos-paper lid. Place in the bottom of the beaker two or three pieces of sodium, each the size of a small pea. Warm the flask *gently*, and soon the evolution of chlorine will begin.

Note the behavior of the sodium. From time to time move the little lumps so as to expose fresh surfaces. When there is no more action fill up the flask with water and set it aside.* Remove the asbestos paper from the bottom of the beaker, and carefully scrape off the substance which has been formed. Dissolve it in the smallest possible amount of water; filter the solution; place it in an evaporating-dish, and evaporate to dryness. Compare the residue, as to taste, color, and behavior on heating, with the residue obtained by the action of hydrochloric acid upon sodium hydroxide. Also compare the two as to the shape of their crystals, as follows: Take two *clean* watch-glasses. In one put about six drops of a water solution of the substance obtained in the last experiment. The solution should be nearly saturated. In the other put the same amount of a similarly prepared solution of the substance obtained by the action of hydrochloric acid upon sodium hydroxide. Warm both watch-glasses until a fine white line of minute crystals appears at the margin of the the liquid in each watch-glass.* Then allow to cool, and crystals will separate, perhaps rather slowly. Examine these crystals with a lens, or with the naked eye if they are large enough. Do the results of this experiment confirm your conjecture or not?

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* If the laboratory is not well ventilated, or if the class is very large, this experiment would better be relegated to the lecture-table. If the labortory is well ventilated, it can be carried out without serious inconvenience.

If you are correct, what is the relation between this substance and hydrochloric acid? Can you now form any idea as to what happens when nitric acid acts upon sodium hydroxide? What would the product contain if it were related to nitric acid in the same way that the substance just studied is to hydrochloric acid? Consider similarly the case of sulphuric acid.

Sum up now, fully and clearly, in your notes, the facts, so far as your experiments have revealed them, concerning these three reactions. Do not attempt, in so doing, to overstep the point where facts end and conjecture begins. Distinguish carefully between what is fairly certain, and what is probable. Aim to mass the evidence in the case so that it will be perfectly clear in its bearing and significance. See that every fact is put in its proper light, and has its full weight.

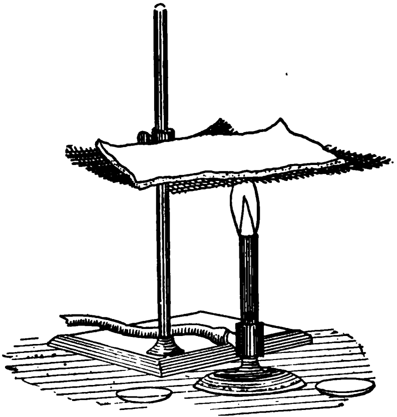

FIG. 38.

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* A good way to do this is to arrange the ring-stand with wire gauze and asbestos paper as shown in Fig. 38; the burner being placed as shown. The two watch-glasses are placed upon the desk under the ring-stand. The hot air from above will evaporate the solutions as rapidly as need be.

LECTURE 24.

THE three reactions we have been studying are important and interesting, because they are representatives of a great class of reactions. When an acid acts upon a metallic hydroxide the products have always the same general character. The same is true of the action of the metallic oxides upon acids. Indeed, with your present experimental resources you could not distinguish, by a simple study of the products, any difference between the behavior of an oxide and an hydroxide toward acids.* In either case there appears water and a substance related to the acid in the same way that the sodium compound obtained by neutralizing hydrochloric acid with sodium hydroxide is related to hydrochloric acid.

We might go on and study in the same way a great many more reactions of this type. If we did, we should always come, in the end, to results of the same order—that is, we should gain, in each case, as a result, a very general qualitative knowledge of the reaction. We should gain no accurate ideas as to the constitution either of the reacting substances, or of the products. We cannot afford to rest content with this partial knowledge. We must try to keep up to the standard of thoroughness and completeness attained in the study of the reaction between hydrogen and oxygen. Consider how vastly more complete is our knowledge of that reaction than of the present one. There we know the constitution of the reacting molecules, and the number of hydrogen and oxygen atoms which unite to form the new water molecule. In order to show this more graphically, let us try to represent the reaction in a form in which the eye can easily take it in. Let us represent *the hydrogen atom* by the letter H, and *the oxygen atom* by the letter O: then the action between hydrogen and oxygen can be pictured in the following manner, which tells at a glance all we have learned about the matter:

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* In such reactions it is probable that a very little of the oxide is first converted into an hydroxide by the water. This then reacts with the acid present. More oxide is then attacked by the water, and so on.

$$2H_2 + O_2 = 2H_2O.$$

We have represented the hydrogen molecule by H_2, writing the 2 a little below and to the right of the H. The molecule of oxygen is similarly represented The molecule of water contains, as we have seen, two hydrogen atoms and one oxygen atom, and its constitution is represented, therefore, by H_2O.

This method of representing molecules so as to indicate the kind and number of atoms in the molecule is exceedingly convenient; and the reaction before us will serve very well to show how it assists us in keeping our results clearly in mind. It must, however, be remembered that its most valuable feature consists in this—*that it represents to us the results of experiment.*

First of all it reminds us that when gaseous hydrogen and oxygen are caused to unite, they form water and nothing else. Secondly, it tells us the number of molecules of hydrogen and of oxygen reacting, and the number of water molecules formed. Again, it expresses the fact that the volumes of gaseous hydrogen and oxygen actually reacting are as two to one, and that the gaseous water formed, occupies the same volume as the hydrogen did.

Finally it serves to remind us of the weight proportions in which hydrogen and oxygen react to form water. We know by experiment the ratio between the weights of the molecule of oxygen and the molecule of hydrogen, or, what is the same thing, the ratio between the weights of the atom of oxygen and the atom of hydrogen.

That is, we know the weight of the oxygen atom, referred to the hydrogen atom as a standard. It will be remembered that this is called the *atomic weight* * of oxygen, and its numerical value is 16: that is, the atom of oxygen weighs 16 times as much as the hydrogen atom.

Since the water molecule contains two hydrogen atoms each weighing 1, and one oxygen atom weighing 16, the *molecular weight* of water is 18.† We will now rewrite our reaction as follows:

$$\underset{\underbrace{2 \times 2}_{4}}{2H_2} + \underset{\underbrace{2 \times 16}_{32}}{O_2} = \underset{\underbrace{2 \times 18}_{36}}{2H_2O}$$

And it now tells us that 4 grams of hydrogen require exactly 32 grams of oxygen (or, what is the same thing, that 1 gram of hydrogen requires 8 grams of oxygen), and that there will be formed 36 grams of water for every 4 grams of hydrogen burned. It is clear that we can, with these figures before us, calculate the weights of hydrogen and oxygen needed to form any given quantity of water. Similarly we can calculate the weight of either hydrogen or oxygen that can be obtained from a given weight of water.

Now wherein is our knowledge of the reaction that takes place between hydrochloric acid and sodium hydroxide incomplete? In the first place our substances are in water solution and not in the gaseous form; and hence we have no direct way of determining the number of reacting molecules of each substance. In the second place we do not know the constitution of both the reacting molecules. We do know the constitution of hydrochloric acid.‡ It yields on electrolysis equal volumes of hydrogen and chlorine; and when equal volumes of hydrogen and chlorine are brought together and ignited, or by any means whatever caused to unite, hydrochloric acid is formed, and the weight of this product is exactly equal to the combined weights of the hydrogen and chlorine used. Therefore this hydrochloric acid contains in its molecule equal numbers of hydrogen and chlorine atoms. One liter of the gas at 0° and 760 mm. weighs about 1.64 grams. Dividing this by the weight of one liter of hydrogen under the same conditions, we have $\frac{1.64}{.09} = 18.22$. That is, the molecule of hydrochloric acid is 18.22 times as heavy as the hydrogen molecule, or 36.44 times as heavy as the hydrogen atom. Chlorine is 35.5 times as heavy as hydrogen, hence its atom is 35.5 times as heavy as the hydrogen atom. Now if there are equal numbers of hydrogen and chlorine atoms in the molecule, and if the atomic weights of hydrogen and chlorine are 1 and 35.5 respectively, it is clear that there must be one atom of hydrogen and one of chlorine in the molecule of hydrochloric acid, for the weight of the molecule in that case would be 36.5, which is in very close agreement with the actual weight of the hydrochloric acid molecule as above determined (36.44). If we use the abbreviation Cl to represent the chlorine atom, the hydrochloric acid molecule will be represented thus: HCl.

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* See p. 110. ‡ See pp. 103, 104.

† Bear in mind that this has been verified by direct experiment. See pp. 110–112.

We do not, however, know thus far the constitution of the substance we have called *sodium hydroxide,* which is made by acting upon water with sodium. We have good reason to believe it contains sodium, oxygen, and hydrogen, which is the same thing as saying that its molecule contains sodium, oxygen, and hydrogen atoms; but how many of each we have no way of telling.

Nevertheless we *must* acquire this knowledge in some way. Most of the reactions we shall study will be conducted in water solution, and most of the substances we work with will be solids like this same sodium hydroxide. We will now enter, therefore, upon some studies which will give us an insight into the methods by which chemists have been able to solve such problems.

The first thing necessary is that we know the *atomic weights of the elements*. If every case of chemical action is, in essence, simply an action between atoms and atoms, atoms and molecules, or molecules and molecules, and if we know the weight of every kind of atom that enters into a given reaction, we can often draw conclusions both as to the constitution of the resulting molecules, and as to the number of reacting molecules. For example, consider this compound of sodium, hydrogen, and oxygen. If we knew the atomic weight of sodium, we could form some idea of the constitution of the molecule in question, for we could weigh out some sodium and convert it into sodium hydroxide as we have before, and notice how much weight the sodium takes up in the operation. One of these two weights would represent the sodium, the other the oxygen and hydrogen taken up. Further, we could determine the quantity of hydrogen in the substance by weighing out some of it carefully and heating the melted substance with metallic sodium or magnesium in a piece of hard glass tube, when, as we have seen, the hydrogen is given off.* By collecting and measuring the hydrogen we should be able to calculate its weight.

We should then be able to calculate the quantity of sodium and hydrogen in one gram of the substance, and by subtracting from one gram the combined weights of hydrogen and sodium as thus found we should obtain the quantity of oxygen present in one gram: so that we should have a complete analysis of the substance. We could then see whether the quantities of sodium, oxygen, and hydrogen were in the proportion of their atomic weights (indicating that there were equal numbers of hydrogen, sodium, and oxygen atoms in the molecule), or whether some more complex constitution was indicated.

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* See p. 120.

In starting out to determine atomic weights, we work from known atomic weights to unknown ones, just as the Coast Survey determines distances between points on the earth's surface by starting out with carefully measured *base lines*, or known distances.* Our base lines will be certain atomic weights which we can quickly and easily ascertain with sufficient accuracy for present purposes. For example,

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* In Fig. 39 let *ab* be the base line measured. Suppose *c* to be the summit of a mountain visible from both ends of the line. The angles *cab* and *cba* are measured; then, having the side *ab* and the two angles, *cb* and *ca* can be calculated. We can now use *ca* or *cb* as a base line.

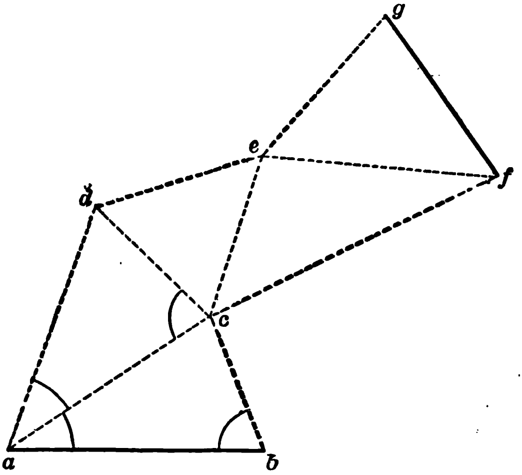

Fig. 39.

Let *d* be another point visible from both ends of *ca*. Measure the angles *dac* and *dca*, and we have the data for calculating *ad* and *dc* and so on. At the end of such a series of triangulations the last line calculated, *df* in this case, is usually measured and its measured length compared with the calculated length as a check upon the accuracy of the measurements.

we know the atomic weights of hydrogen and oxygen through our study of water.

Moreover we can easily determine the atomic weight of chlorine, for it is a gas whose molecule contains two atoms, and in all such cases the ratio between the weights of equal volumes of hydrogen and the gas in question will give the ratio between the atomic weight of hydrogen and that of the element. Since chlorine is 35.5 times as heavy as hydrogen, its atomic weight is evidently 35.5. Nitrogen is another such case. Its atomic weight turns out to be closely 14. Now armed with this list:

H = 1
O = 16
N = 14
Cl = 35.5

let us see how we can contrive to get at other atomic weights. As a good example of methods and reasoning let us take zinc.

It is a solid, and will have to be approached indirectly.

Our object is to bring zinc into action with as many as possible of these elements whose atomic weights we know.

We have many times seen hydrogen appear when zinc is put into dilute acids. What we see is that the zinc disappears and hydrogen appears, and that means that zinc atoms pass into the solution in some way, and that hydrogen atoms come out. If, then, we weigh out a certain quantity of zinc and determine the weight of hydrogen obtained by dissolving it in a dilute acid (by measuring the volume of hydrogen collected and calculating its weight), the weight of the zinc and the weight of the hydrogen will be to each other in the ratio of a certain unknown number of zinc atoms to a certain unknown number of hydrogen atoms. If we knew that for every atom of zinc that went into solution a hydrogen atom came out, then, of course, the numbers would be in the ratio of the atomic weights, and we should have:

$$\text{Zinc weighed} : \text{hydrogen weighed} :: \underset{\text{zinc}}{\text{at. wt.}} : \underset{\text{hydrogen}}{\text{at. wt.}}$$

and since we know the atomic weight of hydrogen, we could calculate the atomic weight of zinc. As a matter of fact we do not yet know that the case is so simple; but in the absence of knowledge we may, if we choose, assume that it is, and see to what result it leads.

The following considerations will point out a method by which we can bring zinc into union with chlorine also. When zinc is brought into hydrochloric acid, hydrogen escapes, and zinc passes into solution. When all the zinc has disappeared, the solution yields, upon evaporation, a white substance, which is not zinc, but which can be proved to contain zinc. Bearing in mind that all that has left the dish during the action is hydrogen, it seems very probable that the zinc has united with the chlorine. Further study confirms this view. A substance identical in every way with the white substance above mentioned, can be made by the action of chlorine upon zinc; and this leaves no doubt as to the nature of the action between zinc and hydrochloric acid. If now the zinc has united with chlorine, then it follows that a certain number of zinc atoms have united with a certain number of chlorine atoms. The same remarks apply here as in the first case. We do not know that a single atom of zinc unites with a single atom of chlorine, but we will temporarily assume that such is the case.

Finally we can oxidize zinc, either by heating it in oxygen or in the air, or, rather more conveniently, by treating the zinc with dilute nitric acid, evaporating carefully to dryness, and heating the residue to a high temperature. In this way we bring zinc into comparison with oxygen, and we will make the same assumption in this case as in the others.

LABORATORY WORK.

1. *Zinc-Hydrogen.* — About 2 grams of zinc are accurately weighed out, and placed in a 100 c.c. flask provided with a delivery-tube. (No drying-tubes are necessary, of course.) The lithia bottle is filled, inverted, and mounted in the pneumatic trough in its usual position. The small flask is now filled nearly full of dilute sulphuric acid, and the delivery-tube is brought under the mouth of the lithia bottle. When all hydrogen has come off, measure its volume as usual. Calculate what volume this would reduce to at 0° and 760 mm., which will necessitate knowing the barometer-reading and the temperature of the water. Calculate the weight of hydrogen obtained (one litre of hydrogen at 0° and 760 mm. weighs 0.09 of a gram), and finally calculate the atomic weight of zinc, on the assumption that for every atom of zinc that goes in, an atom of hydrogen comes out.

2. *Zinc-Chlorine.*—Weigh out accurately about 2 grams of zinc. Place it in a clean weighed evaporating-dish and add a little dilute hydrochloric acid. When the action slackens, add more acid, and so on until all the zinc is dissolved. (The less acid is used, the less time will be consumed in the subsequent evaporation.) Evaporate the solution *carefully* to dryness. Toward the last the heating must be very gentle, and particular attention to the following details is essential. The residue will first appear as a white, crusty mass, which on further very gentle heating will darken and melt. The safest way to melt it is to allow the flame of a Bunsen lamp to play upon it from above. Care must be taken not to overheat, as the substance *volatilizes* or goes off in vapor if too intensely heated. It must be heated *just barely hot enough* to melt it. Next allow the dish to cool until the hand can just be borne upon it; then set it so that the bottom is in cold water. This will cool it quickly, which is necessary, since the substance absorbs moisture from the air very rapidly. When cool, wipe thoroughly clean; dry, and weigh. Calculate the quantity of chlorine with which one gram of zinc has united; and then calculate the atomic weight of zinc on the supposition that one atom of zinc unites with one atom of chlorine.

3. *Zinc-Oxygen.*—Weigh accurately about 2 grams zinc. Place it in an evaporating-dish and add dilute nitric acid in small quantities at a time, just rapidly enough to keep up the action. When all zinc is dissolved evaporate to dryness, *taking great care not to lose by spattering*. Heat the residue, at first gently, and finally as hot as your lamp will permit. Take care that all portions of the residue are throughly heated. Cool the dish and weigh. Heat again. Cool and weigh as before until the weight is constant. Calculate the weight of oxygen taken up by one gram of zinc; and then calculate the atomic weight of zinc on the supposition that one atom of zinc unites with one atom of oxygen.

LECTURE 25.

THE results of our three sets of experiments evidently do not lead us to the same value for the atomic weight of zinc. The comparisons with hydrogen and chlorine lead to the same result; but the comparison with oxygen leads to a result which is twice as great as that obtained by the two other methods. Our task is now to study these results, and see if we can by any means determine which is the true one.

Note, first of all, that we have assumed all these reactions to take place in the simplest possible manner.

We have assumed that when zinc and chlorine unite, one atom of zinc unites with one atom of chlorine; that when oxygen and zinc unite, one atom of zinc unites with one atom of oxygen; and finally that when zinc acts upon dilute sulphuric acid, every atom of zinc as it passes into solution displaces a single atom of hydrogen. Now evidently this assumption is not a correct one in all these cases. It may be true in case of the zinc-oxygen reaction and false in the other two cases, or it may be true in the zinc-chlorine and zinc-hydrogen reactions, and false in the reaction between zinc and oxygen. Either one of these explanations will bring our experimental results into harmony.

In order to see that this is so, let us re-examine our figures, on the supposition that the zinc-oxygen reaction takes place as assumed, and that the atomic weight of zinc lies near 65. The chlorine and hydrogen reactions lead to results which are only about half as great; but if we suppose the reaction to take place between *one atom of zinc* and *two atoms of chlorine*, the result will agree very closely with the result as obtained from a consideration of the oxygen reaction. For in this case we should have

$$\begin{array}{c}\text{wt. chlorine}\\ \text{taken up}\end{array} : \begin{array}{c}\text{wt. zinc}\\ \text{used}\end{array} :: \begin{array}{c}\textit{twice at. wt.}\\ \textit{chlorine}\end{array} : \begin{array}{c}\text{at. wt.}\\ \text{zinc}\end{array}$$

and this would evidently bring us out with a result just twice what we previously obtained.

In precisely the same way we can bring our hydrogen results into line. If it be true that each zinc atom replaces *two hydrogen atoms*, we have then for the form of calculation

$$\begin{array}{c}\text{wt. hydrogen}\\ \text{obtained}\end{array} : \begin{array}{c}\text{wt. zinc}\\ \text{dissolved}\end{array} :: \begin{array}{c}\text{twice the at. wt.}\\ \text{hydrogen}\end{array} : \begin{array}{c}\text{at. wt.}\\ \text{zinc}\end{array}$$

and this would bring us out with a number twice as great as we previously obtained. We see, then, that the vital question is, whether the formula of the zinc-chlorine compound is $ZnCl$ or $ZnCl_2$.

In order to settle this question it is necessary to resort to a line of experiment to which we have already appealed in other cases. If the atomic weight of zinc be 65 or thereabouts, and if the formula of zinc chloride be taken as $ZnCl_2$, then we can at once see what the weight of such a molecule would be; for we have

$$\begin{array}{lr} & Zn = \ldots\ldots\ldots\ldots 65 \\ & Cl_2 = 35.5 \times 2 = 71 \\ \cline{2-2} \text{and hence} & Zn\,Cl_2 = (65 + 71) = 136 \end{array}$$

If, on the other hand, we choose to take the atomic weight of zinc as 32.+, and the formula of zinc chloride as ZnCl, then we have

$$\begin{array}{r} Zn = 32.+ \\ Cl = 35.5 \\ \hline ZnCl_2 = 67.5 \end{array}$$

Now evidently the difference between these molecular weights is a very decided one; and this suggests that if it were possible actually to convert the substance into a gas at a manageable temperature, we might contrive to weigh a certain measured volume of it and compare its weight with that of the same volume of hydrogen at the same temperature and pressure. From the result we could calculate the molecular weight of the substance. If the determination is good for anything, it ought to show us which of the two calculated values for the molecular weight is correct; and consequently which formula is the true one.

It fortunately happens that this compound of zinc and chlorine can be thus dealt with. Its boiling-point is 730°, a temperature at which the experiment is entirely practicable, though it cannot be conveniently performed upon the lecture-table.

One method for carrying out determinations of this sort has been described already.* In this particular case, and in other cases where the temperature required to vaporize the substance is high, another method is more convenient, and will therefore be described.

In its very simplest form the apparatus required is shown in Fig. 40. It consists of a long, peculiarly shaped tube which has an elongated bulb *A* at the bottom, a small side-delivery tube *C*, and is closed at the top by a cork *D*. The whole tube is enclosed in a larger outer tube *F*. By putting substances of different boiling-points into the bottom of *F* and boiling them by means of a Bunsen lamp placed underneath, the interior of *F* can be kept full of the vapor of the boiling liquid, and the long bulb *A* can thus be heated uniformly and steadily at the temperature of the boiling liquid. For such an experiment as the present one the long tube would be made of porcelain, and its bulb and most of the stem would be enclosed in some form of gas-furnace or in a bath of melted metal which would give the required temperature.

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* See pp. 110–112.

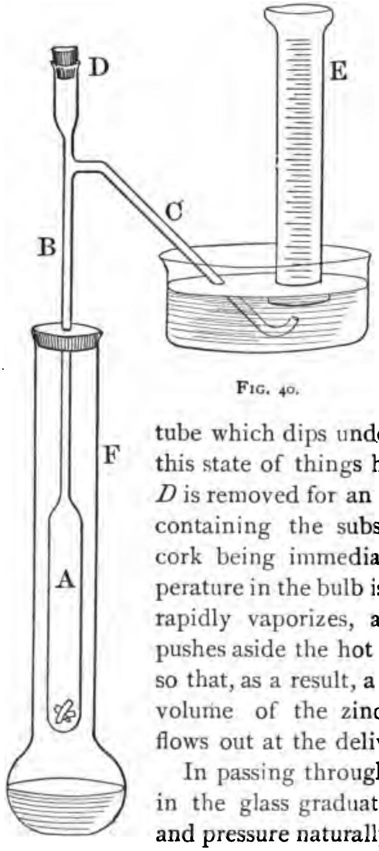

Fig. 40.

In making the determination we have in hand, the first step would be to weigh out accurately a small amount (a few centigrams only) of the compound in a little thin glass tube. Next the long bulb-tube would be immersed in the furnace, and heated until the temperature was constant. This can be seen by noticing when bubbles of air cease to appear at the mouth of the delivery-tube which dips under water as shown. When this state of things has been reached, the cork *D* is removed for an instant, and the small tube containing the substance is dropped in, the cork being immediately replaced. The temperature in the bulb is so high that the substance rapidly vaporizes, and its vapor, as it forms, pushes aside the hot air in the bulb and stem, so that, as a result, a volume of air equal to the volume of the zinc chloride vapor formed flows out at the delivery-tube.

In passing through the water and collecting in the glass graduated tube *E* the temperature and pressure naturally become the same as those prevailing at the time. The substance pushes aside or displaces a volume of *hot air* equal to the volume of vapor formed, but when this collects in the graduated tube it is at the laboratory temperature. The volume of air collected in the graduate is then a measure of the volume which the weighed amount of substance taken would occupy, if it could be gasified at the prevailing temperature and pressure.

We have now determined the volume of vapor obtained and the weight of that volume.

In an actual experiment it was found that 0.0695 grams of this substance yielded 13.6 c.c. vapor, the temperature being 20° and the pressure 716.8 mm. Dividing this by the weight of the same volume of hydrogen at the same temperature and pressure, we obtain 66.22. That is, the molecule of the substance in question is 66.22 times as heavy as that of hydrogen. Finally, by multiplying this result by two we get the weight of the molecule in terms of the hydrogen atom; and this turns out to be 132.4. To which of our calculated values does this result point? Evidently to the first (136); the atomic weight of zinc being 65, and the formula of the compound $ZnCl_2$.

Note clearly, however, that this conclusion is not a perfectly certain one, for there is another way of explaining the result obtained in the last experiment.

Thus the atomic weight of zinc may be 32.5, and the formula of the compound Zn_2Cl_2. This would add up to the same molecular weight as that reached on the supposition that the formula is $ZnCl_2$, and the atomic weight of zinc 65. All we can say at this stage of our study is that the relations involved are explained quite as easily, and more simply, on the supposition that the atomic weight is 65. If the substance could be gasified at a lower temperature so as to be more easily handled, and if we could measure off a given volume of the vapor, and then by some means set free, and measure the gaseous zinc from this given volume of the vapor, we could decide between the two numbers; for if the formula were Zn_2Cl_2, the substance would evidently yield equal volumes of gaseous zinc and chlorine, and the zinc obtained as above would be equal to the measured volume of vapor taken. If, on the other hand, the formula were $ZnCl_2$, then the substance would yield one volume of zinc (gaseous) and *two* volumes of chlorine. That is, the gaseous zinc as separated and measured would be one half the volume of vapor as measured.

Unfortunately the experiment is not one which can be satisfactorily performed, but we shall be safe in holding *provisionally*, the weight 65, waiting to see whether subsequent study will confirm or disprove this value.

Perhaps we may gain some additional light on the problem in hand, by a similar study of some other metal.

LABORATORY WORK.

ATOMIC WEIGHT OF SODIUM.

It is not convenient to bring sodium into combination with oxygen, but we can, as we have seen, cause it to unite with chlorine, to form a white, crystalline substance; and we can do this either by acting directly upon the metal with chlorine, or by first allowing it to act upon water, and then acting upon the solution thus formed with hydrochloric acid.* The latter method will be the more convenient, and it will moreover enable us to bring sodium into comparison with hydrogen at the same time, since in the action of sodium upon water we have hydrogen given off as has been seen. This experiment will need a little planning, for the action of sodium upon water is rapid and sometimes violent.

The safest method is to weigh a small piece of lead tubing about 2.5 cm. long and 4 mm. inside diameter, sealed at one end by hammering the edges together. By means of a piece of glass rod, or better a round steel nail filed off to a square end, pack the tube solidly with sodium, which should be in one piece, of the right size and shape to fill the tube, and should be firmly pressed into place.† Next weigh the tube with the sodium it contains. You now have the weight of the sodium taken.

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* See pp. 129–131.

† See Newth, *Lecture Experiments*, p. 1. If the lead pipe is not available, pieces of glass tubing of the prescribed dimensions can be employed, and the results are generally satisfactory. As a measure of caution cover the flask with a towel during the evolution of the hydrogen.

Fit up a 100 c.c. flask with rubber stopper and delivery-tube; and partially fill it with water. Place a fruit-jar or a lithia bottle in position in the pneumatic trough, ready to receive the hydrogen. The delivery-tube being under the mouth of the jar, remove the stopper of the little flask for a moment, and introduce the little tube. At once replace the stopper, and cover the flask with a towel, so that in case of a slight explosion, no harm will be done. When all gas has come off, remove the delivery-tube, and pour out the contents of the flask into a weighed porcelain evaporating-dish. Rinse the flask out with several successive small quantities of water, so that practically all the sodium compound in solution may be transferred to the evaporating-dish. Neutralize the solution with hydrochloric acid; then set the dish with its contents over the Bunsen flame, and let it evaporate. (If it boils at all, it must be a very gentle boiling. If time permits, it is better to keep the temperature just below the boiling-point.) While the evaporation is going on, the hydrogen collected may be measured, the barometer-reading and the temperature of the water ascertained, and the volume of hydrogen corrected for temperature, pressure, and tension of water vapor. The corrected volume in cubic centimeters, multiplied by .00009, will give the weight of hydrogen collected.

When the solution in the evaporating-dish has evaporated, dry the residue until the weight is constant. Subtract the weight of sodium used, and the remainder is the chlorine taken up. From the weights of sodium and chlorine which have united, calculate the atomic weight of sodium, on the supposition that the union takes place in the simplest possible way—that is, atom for atom. Make a similar calculation from the weights of sodium used and hydrogen liberated, making use of the same supposition.

LECTURE 26.

In considering the results of the experimental work on the atomic weight of sodium, it is seen that the comparisons with chlorine and with hydrogen lead us to the same numerical result, namely, to a figure two or three units over 20. The question may well be raised whether if we were to make the comparison with oxygen we should meet any new complications. As was previously stated, the comparison is not one that can be easily made by you, but it can be made and the results are available. These results we may well consider in connection with our present ones.

Careful experiment shows that 1 gram of sodium unites with closely 0.347 grams of oxygen.

If we calculate this result on the same basis as before, we have

$$1. : 0.347 :: x : 16 \text{ (atomic weight of oxygen).}$$

Whence $$x = 46. +$$

That is, our oxygen result is twice that to which the chlorine and hydrogen determinations led us. Here again, then, we are confronted with the same question as before, and are fortunately enabled to avail ourselves of the same method of settling it.

This compound of sodium and chlorine is capable of being vaporized, though at a decidedly high temperature, and experiments by the method described in the last lecture have given results which place the molecular weight of this substance a few units above 50.

Recently other methods have led to similar conclusions. Now if the atomic weight of chlorine is 35.5 and the atomic weight of sodium 23, or thereabouts, the weight of the simplest possible molecule would be $35.5 + 23 = 58.5$, which is very close to the experimental value.

Of course the question may be raised whether, after all, the atomic weight of sodium may not be one half of 23, or 12.5, and the formula of the sodium compound with chlorine Na_2Cl. If there were no available experimental results except those now before us, the question thus raised would have to be given considerable weight; for of course such a supposition accords as well with the molecular weight 58.5 as does the simpler supposition that the atomic weight of sodium is 23, and the formula of the compound $NaCl$. It is well to notice, however, that neither of the comparisons we made led us to a result smaller than 23, and this would be found to hold with other sodium compounds we might analyze. We might in some cases be led to higher results, but never to a lower one than 23. As a matter of fact, however, we have a great deal more evidence, some of which will appear as we advance, and it all points to a number very near 23 as the atomic weight of sodium.

Up to about the year 1818, questions as to atomic weights were investigated in much the way we have investigated these two cases; and while the atomic weights of certain elements were believed to be settled by very strong evidence, there were some that were not considered as settled at all; opinions differing as to whether a certain number, or double or treble that number, should be taken as the true relative weight of the atom.

In the year 1819, there appeared a memoir by two French chemists, Dulong and Petit, in which they gave the results of an investigation on the *specific heats** of a number of the solid elements, and called attention to a remarkable relation between the specific heats as determined by them, and the atomic weights as then currently accepted. This relation can best be seen by reference to the following table, taken directly from Dulong and Petit's paper:

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* The matter of specific heat and its determination is supposed to have been explained and made the subject of experiment by the student.

Elements.	Sp. Ht.	At. Wt.	C.
Bismuth.......	.0288	13.30	0.3830
Lead..........	.0293	12.95	0.3794
Gold..........	.0298	12.43	0.3704
Platinum......	.0314	11.16	0.3740
Tin...........	.0514	7.35	0.3879
Silver.........	.0557	6.75	0.3759
Zinc..........	.0927	4.03	0.3736
Tellurium......	.0912	4.03	0.3675
Nickel........	.1035	3.69	0.3819
Iron..........	.1100	3.392	0.3731
Cobalt........	.1498	2.46	0.3685
Sulphur.......	.1880	2.011	0.3780

This is the identical table as published. The atomic weights are referred to *the oxygen atom* instead of to the hydrogen atom as is the modern custom. The interesting point is that the product of the specific heat of an element and its atomic weight is, so far as the table goes, about the same for one element as for another; or, to express the same idea a little differently, this product is very nearly *constant*, the number varying only between 0.3879 and 0.3675; but when more elements came to be included in the survey, it was found that the constancy was not without some exceptions. The fact is that while chemists had been working very much in the dark, up to this time, as to methods by which atomic weights should be fixed, they had very often been right in their final conclusions; so that the instances where this product was not constant were distinct exceptions. Moreover it was at once noticed that the list of elements which showed this remarkable relation, included those whose atomic weights were most definitely settled; and finally, that those elements which showed decided departure from this behavior usually gave a product twice too great, or twice too small: sometimes the variation was not quite so simple.

With these latter facts in mind, Dulong and Petit proposed that in these exceptional cases the atomic weights should be so multiplied or divided that they would come into line with the rest. The proposition seems a bold one at first, and it did not find full acceptance on the part of chemists until about 1860. When the change was finally made, it was largely on account of other considerations.*

At the present time Dulong and Petit's work serves as the corner-stone of our modern system of atomic weights. It has thus far found application only to solid substances, but the majority of the elements are solids; and in the case of liquid and gaseous elements, we have other means of getting at the relative weights of the atoms, as we have already seen.

Now one of the strongest reasons for believing that the results we have reached in working on the atomic weights of zinc and sodium are correct, is found in the fact that the numbers 65 for zinc and 23 for sodium *are in accord with the law of Dulong and Petit.* Taking hydrogen as 1,† the constant number is about 6.5. The specific heat of sodium is 0.2934, and this multiplied by 23 gives 6.75, which is near enough to show us that the atomic weight is not 12.5. Also the specific heat of zinc is 0.0955, and this multiplied by 65 gives 6.2.‡ Here, again, there is no reasonable doubt.

We can now see that it is possible to fix approximately the atomic weight of any solid element, by analyzing one or two of its simplest and most definite compounds, and selecting that result which conforms to the law of specific heats.

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* See Wurtz, *The Atomic Theory*, pp. 52–93.

† All atomic weights employed in this discussion are, of course, given in round numbers.

‡ With the modern system of atomic weights the constant product is about 6.5.

We have already seen how the atomic weights of some of the gaseous elements can be approximately fixed.* As we come to different elements in the course of our studies we shall occasionally put these methods in practice.

LABORATORY WORK.

ATOMIC WEIGHT OF MAGNESIUM.

Fit up the 100-c.c. flask (or a test-tube) with double-bored stopper and delivery-tube. Through the second hole of the stopper pass a piece of glass rod to the lower end of which is attached, by a little rubber band, about 0.2 gram magnesium ribbon rolled up into a bundle. Pull the rod up until the metal is close to the cork. Fill the tube (or flask) $\frac{2}{3}$ full of dilute sulphuric acid. Arrange a jar to collect the hydrogen. Place delivery-tube in position and put the stopper tightly into the test-tube. Push down the rod until the magnesium is under the acid. When all action ceases measure the volume of hydrogen, and calculate its weight as usual. From the weights of magnesium and hydrogen calculate the atomic weight, on the supposition that the reaction takes place in the simplest possible way.

The specific heat of magnesium is 0.2475. How does this affect your result?

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* See pp. 137, 138.

LECTURE 27.

We are now in a position to return to our study of the action of sodium upon water.

We have seen that when sodium acts upon water we obtain hydrogen; the volume obtained depending solely upon the quantity of sodium acting. We have also seen that when the solution containing the sodium compound thus formed is evaporated, and the solid residue heated with sodium (or magnesium), we obtain just as much hydrogen as was evolved during the solution of the metal. In other words, when sodium acts upon water half the hydrogen of the water is evolved and the other half stays in solution united with sodium and oxygen. Our studies on the atomic weight of sodium have shown that when sodium replaces hydrogen, it replaces it atom for atom. We may therefore conclude that when one of the hydrogen atoms of a water molecule is driven out, in the reaction we are discussing, *it is driven out and replaced by a single sodium atom,* thus

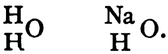
$$\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\mathrm{O} + \mathrm{Na} = \begin{matrix}\mathrm{Na}\\\mathrm{H}\end{matrix}\mathrm{O} + \mathrm{H}.$$

In fact we can hardly be wrong about this, and if we now take into consideration the results of another of our experiments we shall be able to strengthen materially our already very strong chain of evidence. In the experiment in question we weighed out a definite quantity of sodium, caused it to act upon water, evaporated the solution and weighed the residue. Of course the increase in weight was due to the oxygen and hydrogen taken up from the water by the sodium; and we can now see whether these results are in accord with the view that the sodium, hydrogen, and oxygen are present in the proportion of one atom of each. If this is the case, the quantities of the three will be to each other as 23 : 16 : 1. Now in an actual experiment, taken at random, the weights were found to be as follows: sodium 0.5, oxygen 0.37, and hydrogen 0.03; and these weights are to each other as 23 : 17 : 1.4. On our scale of accuracy this is a fairly satisfactory agreement with the calculated proportions given above; and more careful work confirms the result.

Note clearly the exact nature of the argument. We are sure that the compound contains as many hydrogen atoms as it does sodium atoms, and it is all but certain that each molecule contains a single hydrogen atom and a single sodium atom; but whatever view we finally adopt, the results just quoted show that there is one oxygen atom present for every sodium atom (or hydrogen atom) in the molecule; moreover the whole course of our studies upon this subject indicates that the reaction is a simple one, and the facts we have observed find their simplest explanation in the supposition that the molecule of sodium hydroxide is no more complex than is the water molecule.

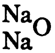
It is, however, obvious that since we cannot volatilize sodium hydroxide at any practicable temperature, we cannot settle the question, as would be desirable, by a molecular weight determination; and hence we must rely upon cumulative evidence from different sources. For the present we shall run no risk in regarding the matter in the simplest possible light, and as we go on we may be able to throw some additional light on the subject by other lines of experiment.

According to our present view, then, the relation between the molecule of water and that of sodium hydroxide is indicated thus:



$$\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\mathrm{O} \qquad \begin{matrix}\mathrm{Na}\\\mathrm{H}\end{matrix}\mathrm{O}.$$

Moreover, since we have found that sodium hydroxide yields, when treated with sodium, just as much hydrogen as was evolved during its formation by the action of sodium upon water, the conclusion seems a fair one that the compound formed by the action of sodium upon dry melted sodium hydroxide, has the formula



$$\begin{matrix}\mathrm{Na}\\\mathrm{Na}\end{matrix}\mathrm{O} \quad \text{or} \quad \mathrm{Na_2O}.$$

This is, in formula, an *oxide of sodium;* and since a substance identical in all respects with that obtained as above can be obtained by the action of oxygen upon sodium, the evidence is complete.

Let us now turn our attention to the other reaction we had under consideration, namely, that between sodium hydroxide and hydrochloric acid. We now know the composition of both the reacting substances. We have strong evidence that the solid, neutral substance obtained on evaporating the neutralized solution, contains nothing but sodium and chlorine,* and that what passes off in the course of the evaporation, is water and nothing else.† It is therefore very probable that the reaction takes place in the following simple manner :

$$\mathrm{NaOH} + \mathrm{HCl} = \mathrm{NaCl} + \mathrm{H_2O},$$

especially when it is remembered that we have established quantitatively as well as qualitatively the constitution of the sodium-chlorine compound.‡

Finally we may take a glance at the reaction between zinc and hydrochloric acid. In this case we have been led to the conclusion that each zinc atom replaces two atoms of hydrogen and unites with two atoms of chlorine. These facts are all expressed in the following equation:

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* See pp. 129–131.

† See pp. 128, 129.

‡ See pp. 148, 149.

$$Zn + 2HCl = ZnCl_2 + H_2.$$

For since the zinc atom replaces two atoms of hydrogen, it will clearly have to react with two molecules of hydrochloric acid instead of one.

We have now studied out these three reactions pretty thoroughly, and have acquired a knowledge of them hardly inferior to that which we attained in our study of the reaction between hydrogen and oxygen; but it will not be practicable for us to continue this style of investigation in the many reactions which we must study in the future; moreover, it is not necessary. The most important feature of these results we have been discussing is that they give us insight into a great many other reactions. The substances we have worked with are representative ones; and each one possesses characteristics which are shared by many other similarly constituted substances.

Hydrochloric acid is a representative of a class of substances called *acids*. Sodium hydroxide represents the *bases*; and the sodium-chlorine compound, which is, as we shall see, closely related to hydrochloric acid, represents the so-called *salts*. Indeed, this substance obtained by neutralizing sodium hydroxide with hydrochloric acid is nothing but *common salt*. It was probably the first such substance known, and as others came to light they were called *salts* because they had some points of resemblance to common salt.

Practically all the compounds we shall study will be either acids, bases, or salts. It is, therefore, very necessary that we get clear ideas as to the characteristic features of each class.

Let us first consider the acids, taking hydrochloric acid as a representative of the class.

Its molecule is constituted thus, as we have seen,

$$HCl.$$

All other acid molecules will be found to resemble it in one respect—they all contain hydrogen, and something else. For example, two other very common and important acids have the formulæ,

Nitric acid HNO_3.
Sulphuric acid H_2SO_4.

In writing these formulæ, it will be noticed that we write hydrogen first; and the result is that the eye at a glance divides the formula of any acid into two parts—the hydrogen and the part which is not hydrogen. This serves to remind us of a fact which a careful study of the acids has established, namely, that in studying any acid we can trace one set of peculiarities in its behavior to the hydrogen, and another set to the rest of the molecule. The power of turning blue litmus solution red, which is manifested by all the acids to a greater or less degree in water solution, is clearly due to the hydrogen, for this is the one substance which is common to all acids. On the other hand, each acid shows, as a rule, some characteristic behavior peculiar to itself, and not shared by other acids, and which can be used as a *test* for the presence of that particular acid, and this peculiarity must evidently be attributed to the part of the molecule which is not hydrogen, since this is different in different acids. Thus hydrochloric acid reddens litmus through the agency of its hydrogen, and the mere observation that a certain liquid showed this behavior would not prove that the liquid was *hydrochloric* acid. To prove this we should have to search for those peculiarities of behavior which are due to the chlorine part of the molecule.

Nitric acid (HNO_3), beside reddening litmus paper,, shows a very characteristic set of peculiarities due to the NO_3 part of the molecule, and similar remarks apply in case of sulphuric acid (H_2SO_4). We will consider some other features of the acids in another connection.

The salts are so closely related to the acids, that we may well consider them next in order.

Taking common salt as representative, and comparing the composition of its molecule with that of hydrochloric acid

$$\begin{array}{r|l} \mathrm{Na} & \mathrm{Cl} \\ \mathrm{H} & \mathrm{Cl} \end{array}$$

the salt appears as derived from acid by the replacement of the hydrogen of the acid by sodium, and we may venture to predict that common salt will show two sets of peculiarities, one set due to the sodium, the other to the chlorine; and further that the behavior of the chlorine will very likely turn out to be the same as appeared in case of hydrochloric acid. This is actually the case, as we shall see. The substance obtained by neutralizing nitric acid with sodium hydroxide is related to nitric acid in the same manner as common salt is related to hydrochloric acid. Its formula is $NaNO_3$, and it can be identified when in water solution only by applying two tests, one of which points out that it contains sodium, and the other of which shows it to contain the NO_3 "group," which is the characteristic feature of the nitric acid molecule and which appears in all its salts. In general every salt is related to some acid in the same way that common salt is related to hydrochloric acid, i.e., the hydrogen of the acid is replaced by one or more other atoms; usually atoms of *metallic* elements; indeed this will be so nearly universally true of such salts as we shall study, that no other possibility need be considered in this connection.

The number of acids with which we shall come in contact is small. Most of them are given below. In the first column is the name of the acid, in the second its formula, and in the third the name which is given to its salts:

Hydrochloric	acid	HCl	Chlorides
Nitric	"	HNO_3	Nitrates
Sulphuric	"	H_2SO_4	Sulphates
Hydrosulphuric	"	H_2S	Sulphides
Phosphoric	"	H_3PO_4	Phosphates
Carbonic	"	H_2CO_3	Carbonates

The name given to any salt always consists of two parts; the first part tells what metal has replaced the hydrogen of the acid, and the second part tells from what acid the salt is derived. Thus common salt is called *sodic chloride*, or often *sodium chloride*. The sodium salt of nitric acid ($NaNO_3$) is called *sodic nitrate*; the sodium salt of sulphuric acid (Na_2SO_4) is called *sodic sulphate*, and so on.

The acids when pure are, as a rule, colorless liquids (sometimes gases), easily soluble in water. The substances we use in the laboratory as "acids" are always water solutions. The bases are solids; usually non-crystalline and only slightly soluble in water. The hydroxides of sodium and potassium are marked exceptions in this latter particular. The salts are solids. The majority are white; some are colored. The soluble ones separate from solution in form of *crystals*, each salt having its particular characteristic crystalline form. In many cases these crystals, though apparently dry, contain a certain fixed and invariable percentage of water. Water thus held in a crystal is called *crystal water*; and careful experiment shows that in every such case there are always present a definite number of molecules of water for every molecule of the salt.

Before we consider the properties of the bases, it will be well to become acquainted with the tests by which we recognize the most common and important acids and their salts, as this will help us very greatly in our future study.

LABORATORY WORK.

The three most common and important acids are hydrochloric, nitric, and sulphuric acids. In order to test a given substance to see whether it contains a chloride, we begin by making, if possible, a clear solution of the substance in water. Next a little nitric acid is added to the solution, and finally a clear solution of argentic nitrate (nitrate of silver). Argentic chloride is formed, and since this is almost insoluble in water, it separates out as a white, curdy *precipitate*, as it is called. The mere appearance of a precipitate is not, however, sufficient. It is necessary to make sure that the precipitate is really argentic chloride. If it turns lavender color on exposure to sunlight, and on further exposure passes through gradually darkening shades of purple, till it is nearly black, and if, before exposure, a portion of it dissolves readily and completely in *ammonia solution*, the evidence is strong enough.

First try the test on a little dilute hydrochloric acid, then on a solution made by dissolving a piece of salt about the size of a match-head in about 10 c.c. of water. Finally try it on solutions about twenty times as dilute, in order to see how the test looks under such circumstances and how delicate its indications are. In careful work, the nitric acid should always be tested to see if it contains any trace of hydrochloric acid. The water used in these tests should always be distilled water, as this is generally free from chlorides, though in careful work this should never be taken for granted. (Try the ordinary water from the faucets.) The reason for adding nitric acid to the solution before adding the argentic nitrate, is that argentic chloride is the only *white* silver salt which is insoluble in nitric acid.

Sulphuric acid, and the sulphates, its salts, can be identified with equal certainty. In order to apply the test, we must have the substance to be tested in water solution. A few drops of hydrochloric acid are added and then baric chloride (barium chloride, $BaCl_2$). The test consists in the appearance of baric sulphate as a white, powdery precipitate, which cannot be redissolved by addition of more hydrochloric acid.

In testing for the presence of nitric acid or nitrates proceed as follows: Mix the solution of the substance to be tested with about its own bulk of a solution of ferrous sulphate (one of the sulphates of iron), then add carefully about 1 c.c. of strong sulphuric acid, pouring it in in such a way that it shall run down the wall of the test-tube and collect in a layer at the bottom of the test-tube. At the junction of the two layers there will appear a ring, which will be brown, as a rule, sometimes showing a quite decided purple tint.

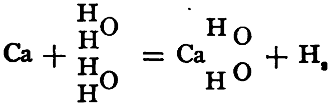
If the substance to be tested is in solution, test it with litmus to see if it is acid. If it is, neutralize with NaOH and filter if necessary before making the test.

LECTURE 28.

THE bases, like the acids and salts, show, as a class, a certain characteristic behavior, which can be traced to a peculiarity in their constitution. In order to see clearly what this peculiarity is, it will be necessary to consider some bases besides sodic hydroxide, which is the only one we have studied thus far in much detail.

Sodic hydroxide has, as we have seen, the formula NaOH. The sodium atom has replaced one of the hydrogen atoms of a water molecule. What would be the result if the metal were capable of replacing *two atoms* of hydrogen? Let us consider such a case. The metal *calcium* acts upon water at ordinary temperatures, producing hydrogen and another substance, some of which dissolves in the water, the rest remaining undissolved. The water solution of this substance turns red litmus blue, and on careful study turns out to have the formula CaO_2H_2.

The nature of the action which has taken place can be easily understood. The calcium atom is capable of replacing two atoms of hydrogen, as shown by methods similar in principle to those described in case of sodium and zinc.* When calcium acts upon water, then, it attacks *two molecules at once*, and replaces an atom of hydrogen in each one, thus:



$$\mathrm{Ca} + \begin{matrix}{}^{\mathrm{H}}_{\mathrm{H}}\mathrm{O}\\ {}^{\mathrm{H}}_{\mathrm{H}}\mathrm{O}\end{matrix} = \mathrm{Ca}\begin{matrix}{}^{\mathrm{H}}\mathrm{O}\\ {}_{\mathrm{H}}\mathrm{O}\end{matrix} + \mathrm{H}_2$$

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* See Lectures 26 and 27.

The calcium atom is here united to two of these OH groups that are left when one atom of hydrogen is abstracted from the water molecule. These groups are called *hydroxyl* groups, and compounds like this calcium compound we are now considering, are called *hydroxides*, and we often treat them as though they were compounds of the elements with this *hydroxyl group*. We usually write the formula of calcic hydroxide $Ca(OH)_2$. Metals whose atoms replace three atoms of hydrogen form hydroxides in which three hydroxyl groups are present; for example, aluminum forms an hydroxide having the formula $Al(OH)_3$.

The hydroxides of the metallic elements are the bases. Those that dissolve in water have the power of turning red litmus blue, but there are very few hydroxides of which this is true. Most of them are practically insoluble in water, and in such cases we must identify them by some other characteristic. When a base comes in contact with the water solution of an acid, there occurs, in every case, a reaction parallel to that which takes place when sodic hydroxide and hydrochloric acid are brought together. The latter reaction runs thus, as we have seen:

$$NaOH + HCl = NaCl + H_2O;$$

that is, there is formed *a salt* (sodic chloride, in this case) and water. This is the characteristic behavior of a metallic hydroxide, or base, and we call the base "strong" or "weak" according as the metal forms definite stable salts, or ill defined and unstable ones. This point we shall work out in more detail later.

For the present the main point to be kept in mind is that every base shows two lines of behavior; one due to the hydroxyl it contains, and one to the metal. And we may sum up at this point the general results of this study of the acids, bases, and salts by saying that while any one single representative of either of these classes, under the most careful scrutiny, and subjected to any kind of physical test, appears to be a perfectly definite homogeneous substance, it acts *chemically* as if it were a double, or *binary* substance, and its whole behavior is a sort of sum of the separate and independent behaviors of its two characteristic parts.

This is particularly noticeable when the substances are *in water solution*, which is a fact of particular interest, since most of the reactions we shall study will be conducted in water solution. It will, then, greatly assist in our future studies if we keep in mind that in water solutions the two parts of an acid base or salt show considerable independence, and can be treated as though they were separate things by themselves. Thus the behavior of a solution of sodic chloride can be best understood by regarding it as containing sodium and chlorine, and not as containing sodic chloride. In recent years this idea has become a ruling one, and we shall see later how it has developed into a much more definite form than that in which it is here stated; for the present, however, this general view of the subject will serve our purpose.

In entering upon a study of reactions between different molecules, we have to consider:

Reactions between acids and bases,
Reactions between acids and salts, and
Reactions between salts and salts.

The most instructive case to consider is the third, since it is the most general.

Suppose we bring together in water solution sodic chloride and potassic nitrate. The result is that we have a solution in which we can recognize by their characteristic behavior

$$Na, Cl, K, \text{ and } NO_3.$$

If we mix water solutions of potassic chloride and sodic nitrate in a similar manner, it is clear that we have present just as before

$$Na, Cl, K, \text{ and } NO_3,$$

and in fact we have excellent experimental evidence that it makes no difference in the final condition of things, whether we dissolve in a given quantity of water (in quantities proportional to their molecular weights) sodic chloride and potassic nitrate or potassic chloride and sodic nitrate. *Notice that in this case all four of the salts concerned are easily soluble in water.* The same general results are obtained in any case in which the conditions are the same as here. Each metal becomes distributed between the two acids present; and, as a result, we have in solution *four salts*, in relative quantities depending upon the proportions in which the two original salts were mixed. These four salts are *in equilibrium with each other*, an exceedingly rapid interchange being constantly in progress.

But the case is totally different if one of the new salts formed by the interchange of the acid and metal parts of the salt is of such a nature that it is removed from the field of action as fast as it is formed.

Take, for example, the reaction used in testing for the presence of a chloride. When sodic chloride and argentic nitrate, both very soluble salts, are brought together in water solution, there are present

$$Na, Cl, Ag, NO_3,$$

and the two new possible salts would be $AgCl$ and $NaNO_3$. But $AgCl$ is practically insoluble in water and as fast as formed separates out from solution. What is the result of this? In the former case we had a condition of equilibrium between $NaNO_3$, KCl, KNO_3, and $NaCl$, in the maintenance of which all four components, Na, Cl, NO_3 and K, were bearing a part. In the present case the constant removal of the argentic chloride makes such a condition of equilibrium impossible. When a little argentic chloride has formed and separated, the condition of things is nearly the same as it was before any had formed; and there is no reason, therefore, why the formation and removal of this substance should not go on indefinitely so long as the necessary constituents, Ag and Cl, are present in the solution. When either one of them is used up, of course the action stops.

The reaction by which we test for the presence of a sulphate is another of exactly the same kind. Here the reacting substances are baric chloride, and perhaps sodic sulphate. Then we have in solution

$$\begin{array}{c|c|c|c} \mathrm{Ba} & \mathrm{Cl} & \mathrm{Na} & \mathrm{SO_4} \\ & \mathrm{Cl} & \mathrm{Na} & \end{array}$$

and were it not for the insolubility of baric sulphate, four salts would exist in the mixed solution in a state of *mobile* or *dynamic* equilibrium with each other as in the case just discussed. The baric sulphate, however, leaves the field immediately, and therefore the formation of this substance goes on until either the barium or the SO_4 is exhausted.

The same general effect is produced if one of the possible products is a gas at ordinary temperatures, for it usually leaves the solution with effervescence as soon as formed, and the reaction runs on until one or both of the reacting substances is used up.

There is one other way in which a substance can remove itself from the field of action, but in order to understand it we shall have to study the behavior of acids, bases, and salts in water solution, somewhat more carefully, and this will involve going over a little history.

LABORATORY WORK.

In order to see the practical results of this kind of reaction—that is, where two salts meet in water solution—try the following cases:

1. Sodic chloride and potassic sulphate.
2. Cupric chloride and magnesic sulphate.
3. Baric chloride and sodic carbonate.
4. Calcic chloride and sodic carbonate.
5. Magnesic nitrate and calcic chloride.
6. Zincic sulphate and sodic phosphate.

Proceed as follows in each of these cases: Prepare *clear* solutions of the two salts in separate test-tubes. Add one solution to the other little by little, shaking or stirring the solution at intervals. If anything separates (or *precipitates*) from the solutions, continue the addition until, on filtering a little of the mixture and adding a drop more of the solution that caused the precipitate, no turbidity results. Then filter the whole mixture. Of course this work is simply intended to give an opportunity to see how such operations actually look.

LECTURE 29.

In the year 1887 Svante Arrhenius, a Swedish chemist, expressed the opinion that the known facts relating to the reactions between acids, bases, and salts could best be explained by regarding these substances as more or less separated (or *dissociated*) into their characteristic parts (or *ions*) when in water solution;* thus hydrochloric acid in water solution would be regarded as dissociated into the two ions

H and Cl;
Nitric acid into H and NO_3;
Sodic chloride into Na and Cl;
Sodic sulphate into $\left.\begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix}\right|$ and SO_4;

and so on.

It is impossible to state here all the facts which have led to this conclusion. They are numerous and weighty. The following are some of the most important:

1. The acids, bases, and salts in water solution behave as though their constituent parts were largely independent of each other. This has always been recognized more or less in case of the salts, and we have seen that it is also noticeable in case of the acids and bases.

2. Numerous careful experiments led F. M. Raoult, in

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* See Nernst's *Theoretical Chemistry* (trans. by C. S. Palmer), pp. 305–312, 421, 424, 428–431, 437–442; Ostwald's *Foundations of Analytical Chemistry* (trans. by G. McGowan), pp. 46-70; Ostwald's *Solutions* (trans. by M. M. P. Muir), pp. 189, 246.

1884, to the conclusion that *the number of degrees by which the freezing-point of a given solvent is lowered, or the boiling-point raised, by the solution of one molecular weight in grams (or one "gram molecule") of any substance in a given weight of that solvent, is constant.* There were some exceptional cases, and these will be noticed presently. The statement given above is interesting because, as Raoult pointed out, it enables us to determine the molecular weights of many substances which we cannot volatilize. The exceptional cases now to be considered are, however, of special interest to us just at this point.

3. *Most of the bases, salts, and strong acids, in dilute water solution, depress the freezing-point considerably more than other substances do.*

For example, one gram molecule of HCl, NaOH, NaCl, or any base, salt, or strong acid having an equally simple formula depresses the freezing-point of water by twice as many degrees as does a gram molecule of sugar. If, now, it be true that the depression is determined *by the number of molecules of the dissolved substance which are present* in a given weight of the solvent (and there is good evidence that this is the case) then we seem to be forced to the conclusion that one gram molecule of HCl, NaOH, or NaCl, in water solution, *acts as though it were two gram molecules instead of one;* or in other words, as though there were present in the solution twice as many molecules as we thought there were.

4. *In all cases where these abnormal depressions appear the substance is one which conducts the electric current readily.*

The full force of this point cannot be appreciated without some understanding of the action of the current upon solutions. The facts are briefly these: *Water solutions* of acids, bases, and salts conduct the current; solutions of other substances (sugar, for example) as a rule do not.

When the current passes through a solution of a salt like cupric sulphate, the solution does not simply transmit the electricity as a copper wire does, without itself undergoing any change. On the contrary, it appears to be an essential condition that the solution shall undergo change.

Here is a U tube filled with a water solution of cupric sulphate. For reasons which will soon be clear, the bend of the U tube is filled with sand which prevents any rapid mixture of the contents of the two limbs. The solution reacts slightly acid toward litmus, as you see. If we immerse the two platinum-plate electrodes from the battery in the two limbs and make the necessary connections, the current passes, and almost immediately two very noticeable things occur. First the negative electrode (the zinc electrode) becomes coated with metallic copper. Of course all one sees is that it becomes covered with a bright red coating, the color and appearance of which suggests copper; but the matter has been very carefully and thoroughly studied, and the substance which coats the electrode is absolutely identical with the substance we call copper from whatever source obtained. Let us now turn our attention to the liquid around the positive electrode. Here no solid substance appears upon the electrode, but on testing with litmus we find the solution strongly acid. Here is a similar U tube which has been exposed for some time to the action of the current. You see the color of the dissolved copper salt is entirely gone. The electrode is heavily coated with metallic copper, and the liquid in the U tube is strongly acid. That the acid is sulphuric acid it is easy to show. Whatever view we may finally choose to adopt as to the precise mechanism of this action of the current, one thing seems clear, and that is that its effect is to send copper to one electrode, and SO_4 to the other.

That is, if the liquid round the positive electrode begins to become acid just at the same time that the other electrode begins to coat with copper, it seems probable, in fact almost certain, that the acidity is in some way brought about by the SO_4 part of the $CuSO_4$ either directly or indirectly. The case of cupric chloride is simpler. If we fill a U tube like this one with a solution of the chloride of copper, and send the current through it as we did in the last case, copper appears at one electrode and chlorine at the other. Here the same conclusion seems warranted, namely, that the action of the current has been to cause the copper to travel to one electrode and the chlorine to the other.

Recall also the action of the current upon a water solution of hydrochloric acid. When the current passes, hydrogen gas appears at one electrode and chlorine at the other. The case of water is more complex. Pure water does not conduct the current, at least not practically. That is, when the electrodes of an ordinary-sized battery are brought into pure water, no easily measurable amount of current passes, and no measurable quantities of hydrogen and oxygen appear. In order to decompose water by the current, it is mixed with sulphuric acid, before the battery is connected, and under these circumstances the hydrogen and oxygen appear. We know they do not come from the sulphuric acid, because no matter how long the current runs, not a trace of sulphuric acid is lost; and though we can obtain hydrogen and oxygen by the liter by this method, the sulphuric acid is the same qualitatively and quantitatively at the end as at the beginning. We will study this in more detail later.

For the present the most important point is that all this is in excellent accord with the idea that bases, salts, and acids act as if their two characteristic parts were more or less independent of each other in water solution. Now bringing together the facts we have thus far considered—

1. That the bases, acids, and salts in water solution conduct the current readily;

2. That most of these substances give abnormally high freezing-point depression when in water solution—

it will be seen that these facts can be explained on the assumption that bases, acids, and salts are dissociated, in water solution, more or less completely, into *electrically charged ions.*

According to this idea, a salt solution of ordinary strength consists partly of sodium ions charged with positive electricity, partly of chlorine ions charged with negative electricity, and partly of undissociated, electrically neutral sodic chloride molecules. The more dilute the solution the greater will be the proportion of the salt which is dissociated. When the electrodes of a battery are immersed in the solution, the positively charged ions are attracted by the negatively charged electrode, and *vice versa;* the result is that each ion travels to the electrode that attracts it, and there its electric charge is neutralized by the opposite electricity of the electrode. When the ions thus give up their charge they at once return to their ordinary state.

When, for instance, hydrochloric acid is decomposed by the current, the hydrogen ions travel to the negative electrode, and there, parting with their charge, pass back into the state of ordinary hydrogen, which, being difficultly soluble in water, appears in the form of bubbles on the electrode. The same is true of the chlorine which travels to the positive electrode. On giving up its charge it returns to the state of ordinary molecular chlorine, which, being only moderately soluble in water, soon begins to appear in the form of bubbles on the positive electrode.

In general, whenever the electrodes of a battery are brought into a water solution of an acid, base, or salt, there is always primarily the same type of behavior. The practical results vary, because the ions frequently enter upon other reactions as soon as liberated. For example, solutions of sodium salts when electrolyzed yield *sodium* at the negative pole, but this at once liberates hydrogen from the water, and passes into solution as NaOH. If the salt be sodic sulphate, the SO_4 part of the salt goes to the positively charged electrode. On giving up its electric charge the SO_4 which appears to be incapable of separate existence except as an ion, at once reacts with the water, forming sulphuric acid and liberating oxygen. If the solution be stirred constantly so that the sulphuric acid and sodic hydroxide formed at the two electrodes are kept mixed, the result is that the composition of the solution is the same at one minute as at another, for the acid and alkali react to form the original substance with which we started, i. e., sodic sulphate. So the general result is that by the electrolysis of such a solution we get oxygen at the positive electrode, and hydrogen at the negative, and the sodic sulphate is the same at the end as at the beginning.

The case is much simpler when we consider salts of such metals as do not decompose water at ordinary temperatures. Such cases will be considered in connection with these metals when we come to study them.

The following statements are intended to put in a simple, compact form the facts which are of most service in the study of simple reactions in water solution.

1. In any water solution of an acid, base, or salt, the ions are usually partly free and partly combined in electrically neutral molecules, but it must be remembered that we are here dealing with another case of equilibrium between two directly opposite actions, just as in case of salt in contact with its own saturated solution, or water in contact with its own vapor in a closed vessel. Thus in a water solution of sodic chloride of ordinary strength, two reactions are in constant operation :

$$\mathrm{NaCl} = \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{Cl}}$$

and

$$\overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{Cl}} = \mathrm{NaCl}$$

When the salt first goes into solution the first reaction prevails; but as sodium and chlorine ions accumulate in the solution, their encounters become more frequent, and the more encounters, the more chances there are for the formation of electrically neutral molecules. The result is that a point is finally reached when just as many molecules are being split up in a given time as are being built up, and under these circumstances we have identically the same kind of equilibrium as in the cases just cited.* Moreover, since the number of encounters between the free ions depends upon the number of them in a given space, it follows that in strong solutions the proportion of undissociated molecules will be greater than in dilute solutions. That this is actually the case there is abundant experimental evidence. The extent to which dissociation takes place depends somewhat upon the temperature. In some cases substances in solution are more dissociated when hot than when cold, most of the common acids, bases, and salts coming under this head. In other cases the reverse is true. No simple and general statement can at present be made as to the effect of temperature upon the degree of dissociation. For our present purpose, however, this is not an important matter.

2. The salts show great uniformity in their dissociation. The salts of the simplest type—that is where a single hydrogen atom in an acid is replaced by a single atom of a metal—are all dissociated to about the same extent. In solutions of average strength more than half the salt is dissociated. This uniform behavior of the salts will be found to be a very important fact as we begin to study reactions in which salts take part.

3. The acids, on the other hand, are dissociated to very different extents. In comparing them in this respect we must be careful to compare solutions *containing the same number of gram molecular weights per litre*, or *equi-molecular solutions*, as they are called.

Hydrochloric, nitric, and sulphuric acids are the most strongly dissociated of the common acids. They are rather more strongly dissociated than the salts.

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* See also Lecture 8.

Phosphoric, sulphurous, and acetic* acids form another group by themselves. They are dissociated to the extent of about ten per cent in ordinarily strong solution.

Finally we have hydrosulphuric, hydrocyanic, and carbonic acids, which are less than one per cent dissociated.

4. The bases may be divided into two classes.

In the first class come the hydroxides of sodium and its near relative, potassium; these are dissociated about as strongly as are the salts.

In the second class come the hydroxides of metals other than sodium and potassium. They are usually only slightly soluble in water, and, since their solutions are very dilute, they are probably mostly dissociated.

5. Free ions as such never leave a solution. They have to pass through the undissociated stage first (except in case of electrolysis. See p. 172); thus, if we have a solution of common salt, so dilute that practically all the salt is dissociated, and if we evaporate this solution, we finally get the original salt we dissolved; and this is because as the solution gets stronger the dissociation lessens, as we have seen; and when the solution becomes saturated it is the undissociated molecules that build up the crystals which we see separate out.

6. Except in a few rare cases undissociated molecules are chemically inactive. That is, the reactions we shall study are mostly reactions between ions; therefore when a substance passes from the dissociated to the undissociated state it must be regarded as having retired from participation in the reaction.† This is an exceedingly important point, as we shall presently see.

In entering upon the study of the elements and their compounds, we shall find this dissociation idea of assistance in explaining some facts which will be brought to our notice.

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* Acetic acid has the formula $H(C_2H_3O_2)$. It is the acid of vinegar.

† All that is meant by this, is that so long as a molecule is undissociated the only reaction in which it takes part is the dissociation reaction.

In a great many cases, however, we can reach our results without its aid.

LABORATORY WORK.

1. If battery or dynamo current be available, try the action of the current upon the following water solutions:

Sodic sulphate,
Hydrochloric acid,
Sodic hydroxide,
Sugar.

Use in each case a U tube with the bend filled with clean white sand. In each case see how the solution is changed by the current, and recognize such of the products as you can.

LECTURE 30.

In Lecture 28 we began the study of three classes of reactions, which three classes include about all cases we shall be likely to meet, namely, the reactions between

Acids and bases,
Acids and salts,
Salts and salts.*

It was there pointed out that a substance could leave the field of action in at least two ways; either by *precipitating*, or separating out from the solution as a solid; or by passing off as a gas. At the end of that lecture the following remark was made: "There is one other way in which a substance can be removed from the field of action; but in order to understand it, we shall have to study the behavior of acids, bases, and salts in water solution more carefully, and this will involve going over a little history."

We have now been over that history, and have gained some idea of the condition of acids, bases, and salts in water solution. We can now return to our study of reactions where we left it, and see what this third way of leaving the field of action may be.

If, as appears to be the case, the ions are the real reacting substances, and if the undissociated molecules are inactive,† then if a substance which is dissociated either very slightly or not at all be formed in a reaction, the case will be like those in which the product was a gas or an insoluble substance. That is, the reaction will complete itself. Water is such a substance: It is dissociated only to the very slightest extent. Therefore in simple reactions where water is one of the products, we have a case where the reaction will run on until one of the reacting substances is exhausted. When we come to study the action of acids upon bases we find a case in point.

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* See pp. 164, 165.

† See p. 175. Keep clearly in mind that all that is meant here is that an undissociated molecule must dissociate into ions before it can take part in any of the reactions we are now studying.

When, for example, sodic hydroxide and hydrochloric acid are brought together we have in solution the ions

$$\overset{+}{\mathrm{Na}} \quad \overset{-}{\mathrm{OH}} \quad \overset{-}{\mathrm{Cl}} \quad \overset{+}{\mathrm{H}},$$

but the hydrogen and hydroxyl ions at once form undissociated water and the reaction runs on. The result is, that we finally obtain a water solution of sodic chloride. We commonly write the reaction thus:

$$\mathrm{NaOH} + \mathrm{HCl} = \mathrm{H_2O} + \mathrm{NaCl},$$

as we have previously seen. Any other acid-base reaction has the same characteristics.

Turning now to the action of acids upon salts, we meet at once more cases in point. If an acid be brought in contact with a salt of another acid, what takes place depends upon the relative extent to which the two acids are dissociated. Let us consider a particular case. Suppose we bring sodic acetate in contact with hydrochloric acid. The ions in solution are

$$\mathrm{Na},\ (\mathrm{C_2H_3O_2}),\ \mathrm{H},\ \mathrm{Cl}.$$

Acetic acid belongs to the class of acids which we call *weak* acids; that is, it is weakly dissociated, and the result is, that as soon as the two ions of acetic acid meet in the solution, they unite and form the slightly dissociated acetic acid $H(C_2H_3O_2)$. So the reaction

$$NaC_2H_3O_2 + HCl = NaCl + HC_2H_3O_2$$

takes place to a considerable extent, that is, a large proportion of the sodic acetate is converted into sodic chloride; so that in such cases, though both the products may be soluble, and though no gaseous product may be formed, the reaction may nevertheless be quite complete, *provided one of the products is only slightly dissociated.* Let us sum up these results in a form convenient for practical use.

1. Reactions between acids and bases are always practically complete ones, since the slightly dissociated water is always one of the two products.

2. Reactions between an acid and a salt of another acid are more or less complete, according as the acid formed by the reaction is a strongly or weakly dissociated one.*

3. Reactions between salts and salts are complete when one of the resulting salts is insoluble (or difficultly soluble) in water.

It will be noticed also that we have given no attention to the possibility that three or four kinds of ions may unite. This is such a rare case that it is not worth while to consider it at present. By far the greater part of the compounds we shall study will contain only two different ions.

From what has been said it is clear that in order to be able to predict what will happen when two salts, an acid and a salt, or a base and a salt, as the case may be, come together in water solution, all we need to know is whether the union of any two of the ions present in the solution will result in the formation of a substance which is insoluble, volatile, or weakly dissociated. We have already enumerated the substances which are strongly dissociated, and also those which are weakly dissociated.* We now need some simple statement as to substances which are insoluble ; and such a statement can be put in the following tabulated form, which can be remembered without difficulty.

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* See pp. 174, 175.

SUBSTANCES INSOLUBLE (OR DIFFICULTLY SOLUBLE) IN WATER.

1. Most metallic oxides. Some of them, like the oxides of sodium, potassium, and calcium, act upon water to form soluble hydroxides.
2. Most metallic hydroxides. Sodium and potassium form hydroxides which are easily soluble in water, and there are two or three more which are sparingly soluble.
3. Most metallic carbonates. Here, too, sodium and potassium are exceptional. Their carbonates are easily soluble.
4. Most metallic sulphides. There are about six exceptions, including, as before, sodium and potassium sulphides. The others will be noted as they are met with.
5. Most metallic phosphates, except those of sodium and potassium.
6. The chlorides of silver and lead and one of the chlorides of mercury.
7. The sulphates of calcium, strontium, barium, and lead.

It will be seen from the foregoing statement that most of the metallic bases and salts are insoluble in water and that *hydrochloric, nitric, and sulphuric acids are the only ones whose salts are as a rule soluble in water.* In fact this last statement, with the additional one that the compounds of sodium and potassium are almost universally soluble in water, covers about the whole case; and when one has fixed in mind the three insoluble chlorides and the four insoluble sulphates the matter is in very serviceable form.

One very important use we can make of this material at once is this: we evidently have all the information we need now to enable us to prepare almost any metallic salt we please. If the salt we desire is soluble in water, we can make it by treating the hydroxide of the metal with the right acid. As we have seen, the reaction is sure to be a complete one, since the very weakly dissociated water is always one of the products. This is a very clean method, too, for it yields simply a solution of the required salt in water, from which the salt can be obtained by evaporation. For example, to make sodic nitrate we add to a convenient quantity of nitric acid, sodic hydroxide enough to use up the acid. The result is a water solution of sodic nitrate.

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* See pages 174, 175. The student will do well to tabulate these statements in his note-book for reference.

If, on the other hand, the salt we desire is an insoluble or very difficultly soluble one, we can make it by bringing together, in water solution, two salts which *together* furnish the ions of the insoluble salt in question. Since every salt contains a metallic ion and the ion of some acid, it is clear that one of the salts whose solutions we mix must contribute the metal ion, and the other the acid ion. Suppose, for example, we wish to make the chloride of silver, an insoluble salt. One of our salts must be a *soluble* silver salt, the other a *soluble* chloride. As a soluble silver salt we are surely safe in choosing argentic nitrate, for all nitrates are soluble in water. For the soluble chloride we can safely take sodic chloride, for the compounds of sodium are always soluble in water. On mixing these two solutions we have in solution the ions

$$Ag, \quad NO_3, \quad Na, \quad \text{and} \quad Cl.$$

The silver and chlorine ions, on encountering each other, form the insoluble silver chloride, and, as previously explained,* the result of this circumstance is that we can count upon the completeness of the reaction. That is, if we take a solution of sodic chloride and drop into it the argentic nitrate solution, every bit of argentic nitrate we add is converted into argentic chloride, until the sodic chloride is used up; and we can easily tell when this point is reached.* By the same general method we can make the insoluble hydroxides, or any other insoluble compound.

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* See pp. 165, 166.

In such reactions as these we have just been considering, the products of the reaction are two, one of which is insoluble, the other soluble. Sometimes the soluble one is what we want, and not the insoluble one. For example, sodic hydroxide is, as we shall soon see, a very important and useful substance, and is made in enormous quantities as follows: Sodic carbonate (common "soda") is dissolved in water, and the solution is heated to boiling. Slaked lime (calcic hydroxide) is then added. Now the ions present are

$$\text{Na}, \quad \text{CO}_3,\dagger \quad \text{Ca}, \quad \text{and} \quad (\text{OH}).$$

Calcic carbonate is practically insoluble in water, and accordingly the Ca and CO_3 ions unite to form this compound. In solution there remain Na and OH ions only; and these, on evaporation, yield sodic hydroxide.

We will look at this more carefully later. It is a good example of an occasionally very useful method.

LABORATORY WORK.

Prepare at least one substance illustrating each of the methods described. Keep careful mental track of what you are about, and what you are after. In making a soluble salt we strive to mix the metallic hydroxide and the acid in such quantities that there is none of either left unused. We then evaporate the solution till the salt begins to crystallize out around the edges and on the surface of the solution, when, on cooling, the salt crystallizes out.

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* How?

† This is not strictly accurate, but the error is not an essential one here.

Again, in making an insoluble salt we mix our two solutions as described, when the salt we desire separates out. By filtering we can retain the insoluble salt on the filter-paper, but is that all that there is on the paper? What does the liquid that runs through contain? Is the substance left on the filter pure as it stands? How can it be purified?

All solutions should be filtered before using.

The action of acids upon salts is particularly well exemplified by the following experiments, which can be divided up among the class.

1. Take about one gram of sodic nitrate. Dissolve it in 3 c.c. of water and add about 5 c.c. of dilute hydrochloric acid (1–4). Evaporate to dryness, and carefully heat the residue until all smell of acid is gone. Test a small portion of the residue for NO_3 and for Cl.

2. Dissolve the remainder of the dry residue in 3 c.c. water, add another 5 c.c. of dilute HCl. Evaporate, and test again. Repeat this process until the test for Cl gives no result. Experiment in the same way starting with NaCl and adding HNO_3; then with NaCl adding H_2SO_4; and finally with $NaNO_3$ adding H_2SO_4. In these last two cases evaporate until thick white fumes begin to appear. Keep careful record of your work; and note particularly how many evaporations are necessary in each case. The results will be discussed before the class.

LECTURE 31.

INTRODUCTION TO THE STUDY OF SODIUM.

THUS far we have been engaged in the study of underlying principles and have given attention only to such substances as seemed best calculated to assist in gaining an understanding of the subject in hand. We have now arrived at a point where we may profitably enter upon the study of some typical elements and their compounds. In so doing we shall have an opportunity to apply the principles we have been discussing.

In Lecture 24 it was pointed out that we could distinguish two distinct types of element, the *metallic* element, and the *non-metallic* element. The significance of this distinction will be made clearer by a study of representatives of the two classes; and since it will often be of assistance to compare the two classes, we will first study a few metals and then a few non-metals, instead of undertaking to study one class completely before beginning upon the other; moreover we shall do well to select as our first objects of study elements which represent as completely as possible the chemist's idea of a *metal* and a *non-metal.*

It fortunately happens that there are two metals whose compounds are very abundant and which are admirably representative metals from the chemical point of view, though they do not in all ways accord with the common idea of a "metal." They are *sodium* and its near relative *potassium.* These two substances are in many respects much alike—so much so that by studying either one thoroughly we gain incidentally a very good understanding of the properties of the other. We will begin with sodium.

We have seen and studied its action upon water, and when we remember that the air is always more or less moist it is not surprising that we never find the free metal itself in nature.

It has to be extracted from its compounds, and the only way we manage to keep it after we have prepared it is by placing it under kerosene or naphtha, so as to protect it from the moist air. If we take out a piece and handle it, we find that at ordinary temperatures it is as soft as wax, and can be easily cut with a knife. When thus freshly cut, the surface is seen for an instant to be bright and glittering; but almost immediately it tarnishes. If, however, we cut it under naphtha, the surface stays bright. Its melting-point is 95.6° ; and since the boiling-point of common kerosene is far above this, we can easily melt sodium under kerosene.* The low melting-point of sodium explains why it is so soft at ordinary temperatures. Most metals begin to soften long before they really melt, and sodium, even at the ordinary temperature, is much nearer its melting-point than most of the ordinary metals are to theirs.

When sodium is cooled down by means of a "freezing mixture" it becomes hard and brittle, and its texture becomes more like that of the common metals zinc, tin, etc. When heated in the air, it soon takes fire and oxidizes vigorously. When we wish to keep a sample of sodium which will show its bright silvery lustre, we usually melt some carefully cut pieces in a glass tube, through which is kept passing a current of pure dry hydrogen, and finally seal up the metal in an atmosphere of hydrogen. In this way a sample can be prepared which will keep its lustre for years.† We have already seen that it is lighter than water. Its specific gravity is 0.97. It is used in the extraction of other metals from their compounds. Such metals as magnesium and aluminum, for example, can be obtained by heating their chlorides with sodium, when the sodium seizes upon the chlorine, setting the other metal free. At one time a great deal of metallic aluminum was procured by this process, and the demand for sodium resulted in its manufacture being much cheapened.

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* In illustrating this, use kerosene in which sodium has been kept for some time. Use a clean freshly cut piece of sodium. See that the test-tube is clean and *dry*. Heat gently and slowly until the metal melts.

† Prepare a tube of ordinary soft glass ¾ inch diameter. After cleaning

The very first method by which the metal was obtained was by passing a powerful electric current through moistened solid sodic hydroxide, when small globules of the metal appeared at the negative electrode. The experimenter was Sir Humphry Davy, and the discovery was made in 1807. Later the metal was obtained on a rather larger scale by heating sodic hydroxide to whiteness with metallic iron. At this high temperature the oxygen leaves the sodium and unites with the iron, while the sodium passes off as vapor together with the hydrogen. It was collected by cooling the vapor and allowing

and drying the tubing, draw it down into the shape shown in the figure, only leave the left-hand end of *A* full size. Put into *A* a sufficient quantity of clean, freshly cut sodium and then draw down the left-hand

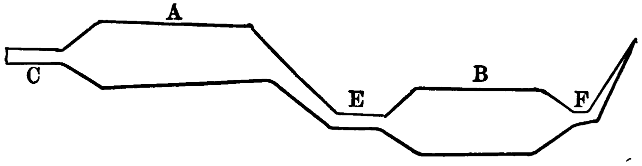

FIG. 41.

end of *A* as shown. Connect *C* with a generator furnishing hydrogen which has been dried by at least two good sulphuric-acid U tubes. When the air has been thoroughly swept out, carefully heat and melt the sodium, and then incline the tubes so that the melted metal runs down into *B*. Seal off at *E* and *F*.

the melted metal, as it condensed from the vapor, to drop into kerosene. At present most of the sodium in the market is made by heating sodic hydroxide with carbon in form of carbide of iron.* The reaction which takes place is

$$6NaOH + C_2 = 2Na_2CO_3 + 3H_2 + 2Na.$$

The temperature required is not very high and the yield is good. The vapor of the metal is cooled and the metal collected in kerosene as in the previous case.

COMPOUNDS OF SODIUM.

The compounds of sodium are very abundant and important. The following will be considered, and in the order given: first the oxide and hydroxide, then the chloride, nitrate, sulphate, and carbonate, these being the most important and interesting compounds.

As to the oxide there is little to say. It can be made by gently heating sodium in the air, or by melting sodic hydroxide with sodium. It is a white powder which melts on heating and which dissolves in water with formation of sodic hydroxide thus:

$$Na_2O + H_2O = 2NaOH.$$

Sodic hydroxide is a very common substance. The commercial name for it is "caustic soda," and its water solution is called "soda lye." The most common method for preparing it is by the interaction of sodic carbonate and calcic hydroxide (slaked lime).

The sodic carbonate is dissolved in water and the slaked lime slowly added until all the sodic carbonate has been converted into sodic hydroxide, according to the reaction

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH.$$

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* Made by heating oxide of iron with pitch to a high temperature in closed crucibles.

The question may well be asked, how can we tell that this has been accomplished? and the answer is that there is a very easy method of telling whether there is any sodic carbonate left in the solution, and the method depends upon a very important fact about carbonic acid (H_2CO_3), which is that it seems to be incapable of existence except in extremely dilute solution. The result is that if, in any reaction, carbonic acid is formed as one of the products, it at once decomposes into water and a gaseous oxide of carbon which has the formula CO_2 and is called carbonic dioxide. The outward and visible sign of this is the so-called *effervescence* which always takes place when a carbonate is treated with an acid, and which is due to the escape of the carbonic dioxide from the solution. In fact if a solution effervesces when mixed with an acid, it generally means that a carbonate is present in the solution, and all that is needed to make the proof complete is to show that the escaping gas is carbonic dioxide. How this can be done will be explained later. For the present we can use this rough test with acid to tell whether we have added enough slaked lime in the reaction we are discussing. Think what the conditions are. In solution there can be only sodic carbonate and sodic hydroxide. The calcic carbonate of course *precipitates*, or separates out as fast as formed. If, now, we filter a little of the solution, and add to this filtered portion a drop of, say, hydrochloric acid, we can easily see if there is any effervescence; if there is, we must add a little more slaked lime, and so on until all the sodic carbonate is used up.

The solution is now allowed to settle; the clear solution is filtered off and evaporated; * the residue is melted, and either broken up into lumps or cast into sticks. Sometimes what is wanted for use is the solution. In this case it is not necessary to evaporate.

The solid substance is white, when pure, and is exceedingly soluble in water. The solution is strongly alkaline, and attacks the skin. When rubbed between the hands it causes the peculiar slippery feeling we describe as "soapy." In the same way it attacks many other animal or vegetable tissues, especially such ones as are oily, fatty, or resin-like in their nature, and this makes it one of the most valuable cleansers we have. It is sent into the market sometimes in sticks or lumps, and sometimes in powder, and in packages of all sizes. Its principal uses are the following:

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* In the commercial preparation of caustic soda the solution obtained as above is evaporated in iron pans.

In Soap Manufacture.—The soaps are simply sodium or potassium salts of rather complex acids, compounds of which occur in most animal fats and oils, as well as in many oils and resins of vegetable origin. When these oils, fats, or resins are boiled with the hydroxides of potassium or sodium, there are formed the sodium or potassium salts of these complex acids.*

These salts usually separate from the solution on cooling. The sodium soaps are solid, waxy substances, without perceptible crystalline form; the potassium soaps are, as a rule, soft and pulpy, and are called "soft soaps." The soaps are, as a rule, rather sparingly soluble in water but dissolve easily in alcohol. Their water solution turns litmus paper blue, which fact points to the presence of hydroxyl ions in the solution. The reason for this will be more fully given later.† For the present it only need be said that whenever a sodium or potassium salt of a weak (slightly dissociated) acid is dissolved in water, the same effect is noticed, namely, that the solution reacts more or less alkaline, and to this extent the solution acts as though it were a weak solution of sodium hydroxide. It is this fact that gives the soaps their usefulness as cleansers. When they are dissolved in water they behave like weak alkali solutions, and when they come in contact with the skin they attack the oily matter which always coats the skin and which holds the dirt. The oily matter is converted by the alkali into a soap which is easily dissolved by the water and the dirt is dislodged at the same time. It will be seen, then, that the "slippery" feeling of a sodic hydroxide solution reminds us of soap for a very good reason, namely, that the soap solution, in so far as it acts as a cleanser, acts through the free alkali, or, more correctly, through the free hydroxyl ions which the solution contains.

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* Good practical directions for making soap on the small scale are printed on the outside of the small cans in which caustic soda and caustic potash are sent into the market.

† See p. 202.

Large quantities of "caustic soda" and "caustic potash" are used, in strong solution, for various forms of rough cleaning; for removing the accumulated grease from the drain pipes of kitchen sinks, and for similar purposes.

Another important industry in which caustic soda finds an application is in the manufacture of *wood pulp* from which paper is made. The wood is cut into chips (or sometimes ground) and treated under pressure, for some hours, with a rather strong caustic soda solution. This attacks the resinous substances of the wood, and converts them into soaps which are soluble in water. The true wood fibre is not attacked by the alkali. When the process is at an end the wood fibre, which forms a pulpy mass, is washed with water to remove the alkali, bleached, and then pressed into sheets which are sent to the paper mills.*

In the laboratory, sodic hydroxide solution is a most useful reagent. The solid substance absorbs moisture with great eagerness and makes an excellent dryer for gases. For this purpose it is broken into small fragments and packed loosely into U tubes. It is also used, as we have seen, in the preparation of other metallic hydroxides.

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* In connection with this industry there has been evolved a new method of making sodic hydroxide on the large scale, namely, by sending a powerful electric current through a strong solution of common salt. Under suitably regulated conditions, three products result: sodic hydroxide, chlorine, and hydrogen. The sodic hydroxide is used in treating the wood as previously described; the chlorine is used in bleaching the pulp. No very satisfactory way of using the hydrogen has been evolved. Sometimes it is passed through naphtha and subsequently used as illuminating gas.

LABORATORY WORK.

Prepare a small quantity of sodic hydroxide. About ten grams of sodic carbonate should be weighed out, dissolved in water, heated to boiling in a porcelain evaporating dish, and converted into sodic hydroxide by the gradual addition of calcic hydroxide (milk of lime). The solution should be tested from time to time as previously described. When completely "causticised" it should be filtered through glass wool, since filter paper is attacked by the solution.

Use this solution in the preparation of a small quantity of soap. For this purpose cottonseed oil, olive oil, or melted tallow can be added to the boiling alkaline solution. Calculate from the reaction* the quantity of sodic hydroxide resulting from the quantity of sodic carbonate taken in the first place. In making the soap add about six times as much oil as tallow (by weight) as you have actual sodic hydroxide in solution. The oil or tallow should be poured in in a thin stream, the solution being kept boiling all the time. After boiling for fifteen or twenty minutes, *keeping up the bulk by adding water*, the solution is allowed to cool. Most of the soap will separate and can be removed as a semi-solid cake. Some, however, stays in solution. In practical soap-making the solution is saturated with common salt, and the soap separates much more completely on cooling.†

When a soap is dissolved in water and treated with a strong acid it behaves as any salt of a weak acid does under such treatment, that is, the weak acid is set free. In case of these soaps there is a double reason, for the free acids are as a rule difficultly soluble in water. Therefore, the soaps are completely decomposed by the strong acids.

Make a few cubic centimeters of a saturated soap solution (hot), and add to it dilute hydrochloric acid, until all the soap is decomposed. (How can you tell when this has been accomplished?) Filter the solution and evaporate the filtrate nearly to dryness, then cool and see if you can recognize what crystallizes out. Note the precipitate on the filter paper. It is the acid with which the sodium was united in the soap.

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* See page 187

† The explanation of this fact will be found on p. 194.

Make a little more of the same strong soap solution. Add to it a clear solution of calcic chloride, drop by drop. What separates is the calcium salt of the acid with which the sodium is united in the soap. "Hard" waters contain calcium salts, and these decompose soaps as you have just seen. It follows that considerable soap has to be used in washing with such waters, and they are objectionable on that account.

LECTURE 32.

COMPOUNDS OF SODIUM, CONTINUED

SODIC CHLORIDE OR COMMON SALT.

THIS substance has been known to man and used by him from the very earliest times of which we have any record. Sea-water contains 2.7 per cent of it; and it is also found in large and important underground deposits in various parts of this country and Europe, as well as in salt springs. Most of the salt in the market comes from these two latter sources of supply and not from sea-water. The salt obtained from sea water by evaporation contains impurities which are objectionable for two reasons: first, they have a bitter taste; and second, they attract moisture from the air and cause the salt to "cake" badly. The salt from salt springs is generally purer.

When large deposits of solid salt, or "rock salt," as it is called, are found, there are two ways of working them on the large scale. One is to sink shafts to the deposit and "mine out" the salt like so much coal; the other is to sink rather smaller shafts, and run water into them. After standing for a while in contact with the salt the water becomes saturated with it, and is then pumped out and evaporated. In any case the product obtained is not perfectly pure. Unfortunately salt is not a particularly easy substance to purify, for reasons that will appear in the course of the laboratory work.

When a small quantity of very pure sodic chloride is wanted for laboratory use, it can be prepared by a method which is interesting theoretically as well as practically. A saturated and filtered solution of crude salt is mixed with about twice its bulk of concentrated hydrochloric acid, or better, a stream of hydrogen chloride gas is led into the solution. In either case a considerable portion of the salt separates out from the solution in the solid state, and very pure.

The dissociation theory seems to offer a pretty satisfactory explanation of this, and many other similar cases where, on the addition of an acid to a saturated solution of one of its salts, the salt separates out more or less completely. If we keep clearly in mind our previous studies on solution and dissociation, the matter will be easily understood.

In order to make it as simple as possible, let us suppose that we have a saturated solution of salt, in contact with some solid salt. Let us further suppose that, in this case, we pass hydrogen chloride gas into the solution.

Now, in the saturated solution, part of the salt is dissociated, and part undissociated, and these two parts are in equilibrium with each other;* moreover, the *undissociated* part of the salt in solution is in equilibrium with the solid salt. When hydrogen chloride is passed in, it dissolves, forming the strongly dissociated hydrochloric acid; that is, a large number of hydrogen and chlorine ions are added to the solution. The result is that this rapid reënforcement of chlorine ions causes the formation of undissociated salt molecules to become more rapid (because there are many more contacts or encounters in a given time), and hence the amount of *undissociated* salt in solution increases somewhat. But this disturbs the equilibrium between the undissociated salt and the solid salt, because the number of encounters between the surface of the solid salt and the undissociated molecules increases, with the result that the solution becomes over saturated, and salt separates from the solution until equilibrium is restored. It is pretty generally true that the addition of any strongly dissociated substance to a solution containing a less strongly dissociated substance, one of whose ions is the same as one of the ions of the substance added, has the effect of causing the former substance, i.e., the weakly dissociated substance, to separate from the solution, and the explanation is essentially the same in all such cases. For example, in testing for the presence of the SO_4 ion we acidify the solution with hydrochloric acid and add baric chloride. Now, if considerable hydrochloric acid has been added, the baric chloride itself will precipitate, as a white precipitate which may be mistaken for baric sulphate. This case is like the one just discussed.

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* See p. 173.

In the same way we obtain our current of hydrogen chloride gas for use in the purification process described above by dropping concentrated sulphuric acid into concentrated hydrochloric acid. This case is similar to the last, only here the undissociated HCl in solution is in equilibrium with the gaseous HCl standing over the saturated solution. The explanation of what happens is the same as in the other case.

In practice we generally add to the saturated salt solution which is filtered and contains no solid salt at all, the strong solution of hydrochloric acid. The result is that the solution becomes over saturated with undissociated salt, and from a solution in this condition the slightest disturbance causes the separation of solid salt, so ultimately the same result is reached as if some solid salt had been in the solution from the first.

Salt is used in freezing mixtures, as we have seen. It is also used in the artificial cooling of storerooms for meat-packing establishments in the following manner: A saturated salt solution, or "brine," is run into a large tank, and cooled, by means which will be described further on, nearly down to its freezing point; then the cold brine is pumped off through pipes which run round the walls of the storeroom. Here is where the low freezing point of a saturated salt solution makes it useful.

Salt is also used as a *preservative*. Most decay is essentially *fermentation*, and is brought about by the life processes of small living organisms called *ferments*. Preservatives are substances in the presence of which these ferments cannot carry on their life processes. It happens that several of the sodium and potassium salts are very valuable in this way. Common salt and potassic nitrate, or *saltpetre*, as it is often called, are important examples. Meat, fish, and other such articles are *corned*, by soaking them in a strong salt brine.

Finally salt is the starting point in the manufacture of other sodium compounds.

Pure sodic chloride melts at about 776° and vaporizes at a bright red heat.

SODIC NITRATE OR CHILE SALTPETRE.

This substance is important as being the starting point in the manufacture of nitric acid. It is found in large quantities in Southern Peru, and is cheaper than potassic nitrate. It is formed in these localities by the decay of animal substances (rich in nitrogen compounds) in contact with calcium and sodium compounds which occur in the soil. The same agencies are at work, though on a much smaller scale, in all soils, and the result is that nitrates not only of sodium, but of calcium potassium and other metals, are present in soils, and become the food of the growing plants—the means by which they get the supply of nitrogen they need for their growth. This change of the nitrogen of decaying animal or vegetable matter into nitrates of whatever metals happen to be present in the soil, is believed to be brought about by a ferment called the *nitrifying ferment*. The nitrogen is particularly available for the plants in form of nitrates, since these are soluble, and hence can be easily taken up by the roots.

In making nitric acid, sodic nitrate is added to concentrated sulphuric acid. In the cold, nothing of much consequence appears to take place. From the reaction

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3$$

it is clear that in the state of equilibrium which will be reached, we shall have in solution the four substances above represented,* since none of them is volatile at ordinary temperatures and none is insoluble. If, however, we raise the temperature, we soon reach the boiling-point of nitric acid, and this begins to distil over. The result is that more nitric acid is formed to restore equilibrium, and the action goes on until all the NO_3 ions have been converted into HNO_3. The reaction, then, is only complete at a temperature where the nitric acid leaves the field as fast as it is formed, and this, indeed, is the main determining factor in the case. It is not the superior "strength" of the sulphuric acid at all, but merely the fact that sulphuric acid has a very high boiling-point—far above that of most of the acid solutions; therefore, the other acid is always the one that leaves the solution when heat is applied, and not the sulphuric acid. This method can, indeed, be generally employed for making acids; and as a matter of fact we do employ it more frequently than any other one method. We simply take some convenient salt of the acid in question, and treat it with sulphuric acid. If the resulting acid is volatile, we heat the mixture and let it distil over. Sometimes the acid is a solid substance, in which case it may precipitate on addition of the sulphuric acid, or it may remain in solution and have to be crystallized out by evaporation.

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* That is, so far as the undissociated part of the solution is concerned.

LABORATORY WORK.

The acids used in the laboratory are, as a rule, water solutions; and the same is true of the alkalies. It will often be convenient to know just how "strong" these solutions are, that is, *just what weight of the "real" acid or alkali is contained in a given volume of the solution.* The first problem, then, is to determine how "strong" the laboratory solution of hydrochloric acid is. It will be remembered that the solution in question is a solution of hydrogen chloride gas in water, and there is no *direct* way of getting an answer to our question; but by making use of some of our past results we can get at a method.

Measure out exactly 20 c.c. of the acid solution into an evaporating dish. Exactly neutralize it with sodic hydroxide solution. What reaction has taken place now? Write it. What does the reaction tell you as to the number of hydrochloric acid molecules that react with one sodic hydroxide molecule? What does it tell you as to the number of sodic chloride molecules formed for every molecule of hydrochloric acid acting? What are the weights of these three molecules? (The atomic weight of sodium is 23.) What relation exists, then, between the weight of hydrochloric acid acting and that of sodic chloride formed? Do you now see that if we knew how much sodic chloride has been formed in this reaction, we could at once calculate how much hydrochloric acid must have been used in making it? How can we find by experiment how much sodic chloride has been formed in the present case? Are you sure your method is practicable? Can you *always* tell how much of a solid you have in solution by this method? What must be true of the substance in solution in order that the method may succeed? Are you sure these conditions are fulfilled in case of sodic chloride? Weigh out *carefully* about 2 grams of pure *dry salt* in your porcelain crucible. Heat the crucible gently for some time with the Bunsen flame. Cool and weigh. Is there any loss? Has the salt undergone any change, either of weight or of properties?

LECTURE 33.

COMPOUNDS OF SODIUM, CONCLUDED.

POTASSIUM AND OTHER METALS OF THIS GROUP.

Sodic Sulphate.—This salt was discovered by Glauber in the seventeenth century, and was for a long time known as "Glauber's wonderful salt," because it was thought to possess remarkable medicinal properties. It is obtained in immense quantities in the manufacture of sodic carbonate. It is, moreover, found in a number of mineral springs, and is one of the products obtained in the manufacture of nitric acid from sodic nitrate. It crystallizes from water solution with considerable crystal water, which it gives up on heating. The dry salt is called *salt cake*. The salt with its crystal water is called Glauber's salt. The properties of the crystals will be studied in the laboratory. The salt is used in medicine somewhat, in the manufacture of sodic carbonate, and in the manufacture of glass.

Sodic Carbonate (*soda, sal-soda, soda-ash, soda crystals, washing soda*).—The use of soda for washing purposes dates back to the time of the early Egyptians. They obtained most of their supply by evaporating the water of certain lakes, and some is obtained from the same source even to-day. It was subsequently obtained from the ashes of certain seaweeds collected on the northwest coasts of France, Scotland, and Ireland. Considerable potassic carbonate, or *potash*, was imported from North America and Russia, where it was obtained from wood ashes, and this, being at that time cheaper, was used for many purposes for which we now use soda. At the beginning of the French Revolution the importation of both these articles was shut off, and it became necessary to devise a new process for its manufacture. It was, moreover, necessary that the materials used should be cheap and accessible, and the process simple and economical. The government offered a prize for the best process, and finally bestowed it upon an apothecary by the name of Leblanc, who submitted a process for manufacturing sodic carbonate from common salt, the other materials needed being sulphuric acid, coal, and limestone—all cheap and abundant. This process alone will be described at present. There are two other very important processes which have been developed in more recent times, but these will be described elsewhere.

The fundamental reactions which take place in the Leblanc process are as follows:

First, the dry salt is treated with concentrated sulphuric acid. Since one of the products is hydrogen chloride gas, the reaction is a complete one, especially if the temperature be raised, and the final state of things is represented by the reaction

$$(1) \qquad 2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

Formerly the hydrogen chloride was allowed to escape directly into the air through tall chimneys; the result was the destruction of most of the vegetation in the neighborhood, and the discomfort of all those living near the alkali works. It was therefore ordered by the government that all but a very small per cent of the gas must be condensed, or in some way prevented from escaping into the air. The remedy adopted was to allow the gas to pass up through chimneys provided with shelves covered with coke, over which water was kept trickling. The gas being very soluble in water, is almost wholly absorbed, and the solution which runs out at the bottom of the tower is what we use in the laboratory now as "crude strong hydrochloric acid."

Thus the alkali works began by cheapening hydrochloric acid, and stimulating all industries involving the use of this substance.

At the end of this first process, then, the salt has all been converted into sodic sulphate, which is ready for the next process; but let us first notice that the sodic sulphate itself is also in demand in glass manufacture and for many other purposes, so here again the alkali process extends its effects to other industries.

The second stage in the Leblanc process consists in converting the sodic sulphate into sodic sulphide; that is, passing from a salt of sulphuric acid (H_2SO_4) to a salt of hydrosulphuric acid (H_2S).

All that is necessary is to abstract the oxygen; and for this purpose it is generally sufficient to heat the substance with something which will unite with *and carry off* the oxygen. One of the most common substances used for this purpose is some form of the element carbon; usually coal, charcoal, or coke. In this case coal is used. The sodic sulphate, or "salt cake," is mixed with ground coal, and heated to a dull red heat for some time. The oxygen is carried off by the carbon as a *gaseous oxide of carbon*, and this is certainly one of the reasons why the reaction works so completely, equilibrium being impossible so long as one of the products is continually being removed. The main reaction is:

$$(2) \qquad Na_2SO_4 + C_4 = Na_2S + 4CO.$$

Finally the sodic sulphide resulting is mixed with ground chalk or limestone (calcic carbonate, $CaCO_3$) and heated, when the mass partially melts and the following reaction takes place.

$$(3) \qquad CaCO_3 + Na_2S = CaS + Na_2CO_3.$$

In practice these last two reactions are carried out together; that is, the sodic sulphate, coal, and limestone or chalk are mixed and heated together for about two hours at a dull red heat. The black or gray-black mass resulting is called *black ash*. It consists mainly of sodic carbonate and calcic sulphide, with some unused coal and limestone, besides undecomposed sodic sulphate. When it is treated with water, sodic carbonate dissolves. The calcic sulphide is insoluble in water; and the rest of the rather numerous constituents of the black ash are as a rule insoluble.

The solution is drawn off and evaporated. If the evaporation be simply carried on until the solution is saturated, the solution on cooling deposits crystals containing considerable *crystal water* (washing soda or soda crystals). (See p. 160.) If these crystals be heated till thoroughly dry we have a white or yellowish-white powder called *soda-ash*.

The main uses of sodic carbonate are:

1. In the manufacture of sodic hydroxide, as has been described previously.

2. In washing. It should be borne in mind that the common hard soaps are the sodium salts of certain very complex but weakly dissociated acids. For example, the most common kind of soap, made from beef fat or tallow (soap grease), has the formula $Na(C_{18}H_{35}O_2)$. When this is dissolved in water the solution reacts alkaline, as we have seen; in other words, the solution behaves like a weak solution of sodic hydroxide. Sodic carbonate, when dissolved in water, reacts alkaline also, and for the same reason, and when its solution comes in contact with the hand it feels "soapy," and acts upon the skin much as a soap solution does; the only difference between them is one of degree.

LABORATORY WORK.

First we will finish finding the strength of our acid and alkali solutions. Evaporate the neutralized solution (see p. 198) *carefully*. Dry the residue to constant weight. Record carefully the weight of dish and contents. Clean and dry the dish and find its weight. The weight of the salt obtained can now be found; and remembering that we know the relation between the quantity of salt produced and the quantity of hydrochloric acid that must have been neutralized to produce it, we can calculate how much real hydrochloric acid (or hydrogen chloride) must have been contained in the 20 c.c. of the acid we measured out, and from this we can calculate how much hydrogen chloride each cubic centimeter of the solution contains. (Calculate and record it.)

A moment's thought will show that we could proceed to find the strength of the sodic hydroxide solution by the same method; but is it necessary to go through with this rather long process? (What would be the process?) Is there not an easier method? Measure out say 15 c.c. of the sodic hydroxide solution into the evaporating dish and neutralize it with some of the same solution of hydrochloric acid previously used, *noting the exact volume of acid solution used in the process.* Remember we know how much hydrogen chloride this measured quantity of acid contains, so we know just what weight of hydrogen chloride has entered into reaction. Look at the reaction once more and see what is the relation between the quantities of hydrochloric acid and sodic hydroxide which just neutralize each other, forming salt and water. Do you not see now how you can calculate how much sodic hydroxide your 15 c.c. of sodic hydroxide solution must have contained? (Calculate and record it.)

Next we want the "strength" of the nitric acid and also that of the sulphuric acid. If we undertake to use the same method we did with the hydrochloric acid, we shall be obliged to make some experiments upon sodic nitrate and sodic sulphate in order to find whether their solutions can be evaporated and the salt dried thoroughly without undergoing any change, just as we did with sodic chloride (see p. 198); but is it necessary to use this method? Why cannot we use a method similar to the one we employed in case of sodic hydroxide; that is, measure out say 15 c.c. of the nitric acid and neutralize it with sodic hydroxide solution, *noting the exact amount used.* Since we have determined the strength of the sodic hydroxide solution we know just how much real sodic hydroxide we have used, and we can easily see from the reaction between nitric acid and sodic hydroxide (write it) what is the relation between the quantities of nitric acid and sodic hydroxide, which just neutralize each other. The rest of the calculation is easy. By a precisely similar method we can find the strength of the sulphuric acid.

We have now three acid solutions and one alkali solution, all of known strength. Such solutions are convenient in many ways. By means of them we can use known quantities of acid or alkali when we please; further, we can use any one of our acid solutions for determining the quantity of sodic hydroxide contained in solutions of unknown strength, and conversely we can use our alkali solution for determining the strength of other solutions of hydrochloric, nitric, or sulphuric acid.

LECTURE 34.

OTHER METALS CLOSELY RELATED TO SODIUM.

If the foregoing studies on sodium have been followed carefully, it will be realized that we have been dealing with an element having very marked points of interest, whether we consider the element alone, or its compounds. The metal is remarkable by reason of its softness at ordinary temperatures, its lightness, and the rapidity with which it decomposes water at ordinary temperatures. If we consider its compounds, the first thing that attracts our attention is their almost universal solubility in water, the abundance and wide usefulness of some of them, the strongly alkaline character of the hydroxide in water solution, and the stability and definiteness of the salts. It will be remembered that in beginning our studies on special elements with sodium, we selected it as a good example of a typical metal, and it may be here emphasized that this last characteristic, namely, the formation of stable, clean-cut, well crystallized salts, is one of the most marked characteristics of what the chemist calls true, typical metallic behavior. The ordinary salts of sodium, particularly those which it forms with the strong acids (HCl, HNO_3, and H_2SO_4), can be dissolved in water without undergoing any change other than that of ionization, and can be obtained again by evaporating the solutions. Some of them carry crystal water, but they can be heated till this is driven off, and the anhydrous salt obtained without difficulty. Its salts with the strong acids are neutral to litmus. Its salts with the weakly dissociated acids, on the other hand, are generally alkaline (witness Na_2CO_3, Na_2SO_3,

Na_2S, Na_3PO_4, the soaps, etc.). It will perhaps be best to postpone the explanation of these latter facts, but it will be well to remember that it is generally true that salts which typically metallic elements form with weakly dissociated acids are generally alkaline, and that these same elements generally form neutral salts with the strongly dissociated acids.

Sodium does not by any means stand alone in the respects we have enumerated. It is merely a representative of what we call a *group* of elements, each one of which shows in a greater or less degree the same characteristics we have particularly noted in case of sodium.

There are four other such elements known at present. Only one of them approaches sodium in the abundance and importance of its compounds; but in other respects the resemblance is striking and suggestive. Placed in the order of their atomic weights, this group of elements stands thus:

Element.	Atomic Weight.
Lithium, Li	7
Sodium, Na	23
Potassium, K	39
Rubidium, Rb	85
Cæsium, Cs	132

All of them decompose water violently, forming soluble and strongly alkaline hydroxides; all of them are soft and waxy at ordinary temperatures; indeed, cæsium, although it has not been prepared in satisfactory quantities, appears to be a liquid at ordinary temperatures, like mercury. All of them are silver-white, and none of them have ever been found in nature in the uncombined state. Another curious fact is, that as we pass from lithium, with atomic weight 7, to cæsium, with atomic weight 132, we find each characteristic feature of the group either intensifying or diminishing as we advance.

But although the degree to which these characteristic properties manifest themselves does vary, the members of this group of elements stand alone in the decided and unequivocal character of their chemical behavior. They have well been called the *alkali metals* on account of their soluble and strongly alkaline hydroxides. Such "groups" are not at all infrequent. In fact, we are practically forced to study the chemical elements by groups, and we get our most suggestive view of them from this method of study. In the present case we have already noted some of the characteristic group properties, and we may now notice some others which we are to look for more or less in all such groups.

1. The corresponding salts of these metals tend to crystallize in the same form. This is very marked in case of the chlorides, where the characteristic form is the cube. The most probable reason is that the crystal form is determined by the arrangement of the molecule, and if this is so, molecules containing the same number of atoms and similarly arranged might be expected to form similarly shaped crystals. This idea was formerly employed with great skill and judgment in the fixing of atomic weights, in cases where question arose as to the replacing power of the metal in question. In such a case, if a metal was found to form a chloride, crystallizing (without crystal water) in cubes, it was considered highly probable that its formula was like that of sodic chloride.

2. The elements of a group usually occur closely associated in nature, and the same is true of their compounds. For example, where large deposits of sodium compounds occur, we also find compounds of the other members of the group, only perhaps in very small amount. This is what might be anticipated. These substances have been, and are still being distributed over the surface of the earth and accummulated in deposits by the agency of water, and it is natural to expect that elements whose compounds are so markedly soluble, stable, and alike in their chemical behavior, will, in the end, be accummulated in much the same places.

3. They all have the same *replacing power;* and their cor-

responding compounds have similarly shaped formulæ. The general formulæ, where X may represent any one of these metals, are:

Oxide	Hydroxide.	Chloride.	Nitrate.	Sulphate.	Phosphate.	Carbonate.	
X_2O.	XOH.	XCl.	XNO_3.	X_2SO_4.	X_3PO_4.	X_2CO_3.	etc.

It has already been stated that the only element of this group whose compounds rival in abundance and importance those of sodium is potassium. Some of the compounds of this element must now be mentioned.

In the first place, metallic potassium has never been of much importance. It can be made by the same methods used in case of sodium, which it closely resembles in appearance and behavior. It decomposes water rather more violently than sodium, and the hydrogen generally catches fire and burns, as the metal floats hissing upon the surface of the water.

The chloride is found in quite extensive deposits in the great salt beds of Stassfurt, Germany. It is very much like salt in appearance and taste. Its crystalline form is the same. It is, however, more soluble in hot water. It is used mainly as a starting point in making other potassium compounds.

The hydroxide is in appearance exactly like the corresponding sodium compound. It is made by exactly the same process, only substituting potassic carbonate for sodic carbonate.

Its uses are the same, the principal ones being in the manufacture of soap and in cleaning.

The nitrate is probably the most important salt of potassium. It was known to the early alchemists, by whom it was called *sal petrae*, or "rock salt," from the fact that it was obtained in those days (and is still, for that matter, in Ceylon and some parts of India) by treating certain porous rocks with water. In fact, one of the most common names for this substance is *saltpetre*, which comes directly from the old name. Another name by which it is known is *nitre*, which is also a remnant of the old alchemical name *sal nitri*. It occurs in the soil, near or on the surface, in hot countries like India, Syria, and Persia, where nitrates are formed by the gradual oxidation of animal matter rich in nitrogen, in presence of alkalies, like soda or potash.

In some countries, like Sweden and Switzerland, this process has been carried on artificially. Refuse animal or vegetable matter is piled up in heaps with wood-ashes or mortar and allowed to "weather" for two or three years. On scraping off the outer layers of the heap, and treating with water, a solution is obtained which, on evaporation, yields potassic nitrate; the salt is then purified and sold. Considerable potassic nitrate is at present made from potassic chloride by mixing it, in water solution, with Chile saltpetre (sodic nitrate); on evaporation the solution yields potassic nitrate, sodic chloride being found in the "mother liquor." The reaction is:

$$KCl + NaNO_3 = NaCl + KNO_3.$$

The reaction depends upon the great difference in the solubility of potassic nitrate and sodic nitrate in cold water. 100 parts of water at ordinary temperatures dissolve 87.5 parts of sodic nitrate and 31.2 parts of potassic nitrate.

It is more expensive than sodic nitrate, and hence cannot be economically used as a fertilizer.

It is extensively used in medicine, as a preservative and in the manufacture of gunpowder.

Gunpowder is nothing but a mixture of charcoal and sulphur with potassic nitrate. The nitrates when heated decompose more or less, and oxygen is one of the decomposition products. This decomposition takes place much more readily and completely if some substance be present which unites with, and removes the oxygen as fast as liberated. If, then, potassic nitrate be mixed with charcoal and sulphur, and heated, the oxygen unites with these two substances, and they burn very rapidly.

The reason for the very rapid burning is the large quantity of available oxygen. Any substance which burns or oxidizes when heated in the air will burn vastly more rapidly when mixed with some substance like potassic nitrate or potassic chlorate. Such experiments are in general dangerous.

Gunpowder is simply one of these mixtures of easily burning substances with such a quantity of potassic nitrate as furnishes the right quantity of oxygen. As to the burning substances to be chosen, they must be fairly cheap, must not be of such a nature as to attract moisture from the air, and must give gaseous products on burning. The power which gunpowder exerts is due to the very rapid liberation of these gaseous products at an enormously high temperature at the moment of burning. In case of gunpowder, these gases occupy about 300 times the volume of the powder, and if the burning should take place in a strong closed vessel which was completely filled by the powder before firing, the pressure exerted by the gaseous products would be not far from 42 tons per square inch. As a rule, however, something gives way long before this pressure is reached.

The gases liberated are principally carbonic dioxide (CO_2), carbonic oxide (CO), and nitrogen.

Sodic nitrate is unfit for use in gunpowder, as it attracts moisture from the air. Potassic nitrate does not.

Potassic sulphate is much like sodic sulphate, only it is very much less soluble in water and not so widely used. It carries no crystal water.

Potassic carbonate, or potash, was originally obtained from the ashes of trees. All plants require potassium compounds as part of their food, and the potassium taken in by the plant is probably present as the potassium salt of some very complex acid rich in carbon. When plants are burned to ashes, these complex salts are decomposed, and potassic carbonate remains as the final product. A great deal was formerly exported from North America and Russia, where it was obtained principally as above described. The washings of raw wool contain potassium salts derived from the perspiration of the sheep, and when these washings are evaporated and the residue *calcined*, or heated to a high temperature, these complex potassium salts are decomposed, leaving potassic carbonate.

In the manufacture of sugar from the beet-root, the juice of the beet-root is evaporated, and the sugar crystallized out. The mother liquor which remains is rich in potassium salts from the beet; and these, when evaporated and calcined, yield potassic carbonate. Finally, some is made from potassic chloride by a process similar to the Leblanc process for manufacturing sodic carbonate.

It is used in making potassic hydroxide or *caustic potash*; in glass manufacture, and for other purposes which will be mentioned in other connections.

It is much more soluble in water than is sodic carbonate, and attracts moisture from the air to such an extent that a dish containing granular potassic carbonate is frequently placed in the balance-case to keep the air dry and prevent rusting of the delicate parts of the balance.

LABORATORY WORK.

Determine how many molecules of crystal water (see p. 160), crystallized sodic carbonate, and crystallized sodic sulphate contain. It is not always true that we can readily determine the percentage of crystal water in a crystallized salt. It depends upon whether the salt will stand the amount of heating necessary to drive off all its crystal water, without itself undergoing decomposition. In case of the two salts we are considering we can heat them to any reasonable extent without decomposing them; and their crystal water is given off with considerable ease.

Weigh out carefully about 2 grams of the crystallized salt in a weighed porcelain crucible. Place the crucible cover so that the crucible shall be nearly but not quite covered, and heat the whole with the Bunsen flame, gently at first, and afterwards as hot as possible, until the weight is constant. Find the loss in weight. This loss represents the crystal water. The difference between the weight of the original salt and that of the crystal water gives the weight of the *anhydrous* (water free) salt. Now we have our data from which to calculate the number of molecules of water present for every molecule of the anhydrous salt. Suppose the salt under consideration is sodic sulphate. The two weights found as above represent sodic sulphate and water, in the proportions in which they were present in the original crystallized salt; that is, they represent one molecule of sodic sulphate and an unknown number of water molecules. It follows, then, that

$$\begin{array}{c}\text{wt. anhydrous}\\ \text{salt}\end{array} : \begin{array}{c}\text{wt. crystal}\\ \text{water}\end{array} :: \begin{array}{c}\text{mol. wt.}\\ Na_2SO_4\end{array} : \begin{array}{c}x \text{ times}\\ \text{mol. wt. water.}\end{array}$$

Work out the calculation and find the value of x (that is, find how many times the molecular weight of water is contained in the number you obtain as the result of the above calculation). Of course the same form of calculation applies to any such case.

Weigh out carefully into clean, weighed watch-glasses about 2 grams each of crushed crystals of sodic carbonate and sodic sulphate. Set them aside where they will be fairly well protected from dust, and weigh them each day until the weight is constant. Then calculate how many molecules of crystal water have been lost, and compare your result with that obtained in the experiment just described.

LECTURE 35.

THE SODIUM GROUP, CONCLUDED.

THE compounds of lithium, cæsium, and rubidium can hardly be mentioned here. Some of the compounds of lithium are used in medicine, and are often found in traces in spring waters and in larger quantities in some minerals. Cæsium and rubidium, on the other hand, are only laboratory curiosities, and have thus far been found in traces in mineral waters and in certain minerals. It has been stated that in general all these compounds, and the metals themselves, are strikingly like the corresponding sodium and potassium compounds.

The last point to be considered in connection with this, our first group, has to do particularly with the fact that we regard them as *elements*. The question naturally arises how we happen to regard these particular substances as elements; and this is, of course, a question which will arise in case of every element we study. We are here confronted with one of the profoundest questions in all chemistry; but it is nevertheless a matter which must be considered even in an elementary course like this, for it involves the more pointed question, what is meant by an element?

It will be remembered that we gave a partial answer to this question, in case of hydrogen, oxygen, and chlorine, in connection with our studies on the composition of water and of hydrogen chloride; * but that was a rather peculiar case.

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* See p. 107.

All the substances under consideration were *gases;* and the reasons there given may not seem to apply so clearly and conclusively in the case of solid elements like the present ones. There is really no essential difference in the facts, and they lead us to the same conclusion in both cases; but there is a difference in the experimental evidence available, and in the particular facts revealed.

The word *element* itself really implies more than it should when applied to the substances so designated by chemists to-day. Such a substance would be absolutely uniform or homogeneous throughout, and it would be impossible to recognize in it, by any means whatever, more than one kind of matter, which is the same thing as saying that its molecule would be homogeneous and contain only one kind of atoms. There is not a single substance known to-day of which this is proved beyond doubt. What, then, is the status of our so-called elements? Simply this; they are a group of substances which mark the coast-line, so to speak, of our knowledge of what a truly simple substance is like. When we were considering atomic weights, the question arose, "if analyses of different compounds of the same element lead to different atomic weights, which shall we take?"* We have given what seems to be a satisfactory answer for present purposes by taking the number which, when multiplied by the specific heat of the substances, gives a number near 6.5; but this is no help to us in answering our present question. When we start to determine an atomic weight, it is assumed that we have exhausted all the resources of modern chemistry on the question whether the substance we are dealing with is to be considered an element; and the mere fact that its specific heat multiplied by its atomic weight gives 6.5, may or may not be significant. For example: several years ago there was recorded, in most text-books, a metallic "element" called

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* In the case of zinc, for example, when we have our choice between 32.5 or 65. See p. 146.

didymium, whose atomic weight had been determined to be 147, and its specific heat 0.04479, giving as a product 6.3, a very satisfactory result. That substance is to-day known to be made up of at least *two* others, and perhaps more. Their atomic weights lie very near together, and their specific heats, of course, lie near together also, so the old result is not hard to understand.

The point is, that while we fix atomic weights to-day by the law of specific heats, *we have no decisive way of determining whether a certain substance is really a simple, indivisible, "elementary" form of matter or not.* We fall back, then, upon cumulative circumstantial evidence. When we say that a substance is considered to-day as an "element," we base our statement upon the same kind of facts as when we say that a sample of sugar is "pure." In this latter case we imply that every bit of the substance in question accords in its properties with all we know about sugar: but when we say that we believe sodium to be an element, we not only imply that it is homogeneous (that is, that its molecules are all alike), but also *that its molecule is homogeneous.* The sugar may be perfectly pure and homogeneous; but we know its molecules to be made up of several kinds of atoms. On the other hand, we believe that the molecule of sodium contains only one kind of atom.

Let us now consider the experimental evidence. First, why do we regard sodium as homogeneous? How do we know when we have sodium? What are the particular properties and characteristics which serve to distinguish it from all other substances?

Its color, specific gravity, specific heat, melting-point, etc., are of course characteristic, but no one of them by itself is enough to characterize sodium sharply. There is, however, one peculiarity of behavior in which the substance we call sodium stands absolutely alone among all substances with which we are acquainted. When it is brought into the non-luminous flame of the Bunsen lamp, and thus heated to a very high temperature, its vapor emits a very brilliant yellow light. We have an instrument called the spectroscope, which enables us to analyze light. White light is composed of all possible shades of color, between a dark violet and a very dark red; and when sunlight is sent through the spectroscope we see before us, as we look into the eye-piece of the instrument, a narrow band of light, violet at one end, red at the other, and all intermediate shades between. If we send any kind of colored light through the instrument, the prism of the spectroscope bends aside the different colored rays of light to different extents; and the result is, that as we look again, we see instead of the ribbon of light of all colors, more or less sharply defined bands or lines of light, distributed in different parts of the space where the ribbon was; and these bands or lines represent the kinds of light of which the colored light was composed. When we send the light from a flame in which sodium is burning through the slit-shaped aperture of the spectroscope, we see, if the instrument is one of moderate power, a single bright yellow band of light, and that is all. In very powerful instruments the line is seen to be actually composed of two yellow lines very close together. *There is no kind of light known except that from glowing sodium vapor which gives this line in the spectroscope.*

When potassium is brought into the flame a lilac-colored light is produced. This tint must, of course, be a mixed one; and we might anticipate that it would contain red rays and blue or violet rays. Analyzed by the spectroscope, it gives two distinct red lines, one of very dark red and another far out in the violet. No other known kind of light gives these lines. They are absolutely characteristic of the substance we call potassium. Lithium, in the Bunsen flame, gives a beautiful dark crimson light. In the spectroscope it shows a brilliant, well-defined red line, and a very faint yellow one. Rubidium or cæsium impart to the flame a color which is almost exactly like that of potassium. The spectroscope, however, shows very different groups of lines in the two cases. In fact, it was the observation that the mother liquor of the Dürkheim mineral water contained a substance which gave lines in the spectroscope differing in number and position from those given by any other known element, which enabled Bunsen, in 1860, to announce the discovery of cæsium. The discovery of rubidium (1861) was similarly accomplished, only the material under examination was a mineral from Saxony. It only needs to be added that every one of our so-called elements gives, under proper conditions, a characteristic set of lines, or *spectrum*, as it is called, and that the salts of the metals do as well for the ordinary tests as the pure metals. Here, then, we have a new and rapid method for finding what elements are present in a mixture.

It is not always sufficient to heat the substance in the Bunsen flame; in fact, most elements give no spectra in the Bunsen flame, but have to be heated in the electric arc or in the spark from an induction coil.

By using a spectroscope combined with an astronomical telescope, we have been able to analyze many of the stars, and to show that they are for the most part made up of the same elements as enter into the composition of the earth. The same is true of the sun, only the method of examining it is somewhat peculiar and need not be discussed here.

We are now ready to consider the question, what is sodium? The best answer seems to be, "It is the substance that gives a certain yellow line in the spectroscope." We believe it to be homogeneous because, when it has been prepared with the utmost care and skill possible, it always gives that line, *and that one only*. The most severe test that could be applied would be to take, say, 500 grams of the purest sodium obtainable, and to distil it—that is, heat it to its vaporizing point, and condense the vapor in perhaps a hundred small successive portions. If each of these portions, when examined in the spectroscope, showed identically the same line and no other, it would confirm our belief in the homogeneousness of sodium. This method exemplified above is called *fractionation*, and it can be applied in a number of ways. For instance, some salt of the metal in question might be dissolved in water, and the solution allowed to evaporate slowly, the crystals being picked out and set aside in separate little lots as they appear.

It was by this means that the metal *didymium* mentioned above was finally shown to contain at least two simpler substances. The nitrate was dissolved in water and allowed to crystallize. The first crystals which separated were pink, the last were green, and the middle fractions were intermediate or mixture tints. This method has been thoroughly applied in only a very few cases.* It is interesting to us at present as being occasionally useful in our search for truly simple substances. One of the very best reasons for regarding a given substance an as element, is found in the definiteness of its compounds and the exactness of their analysis; for this we take to indicate that the atoms of the substance are alike, and that when they unite with, say, chlorine atoms, they form always identically the same molecules; and this means that a large mass of the chloride is made up of molecules, every one of which is exactly like every other. The best way to test this point in the case of sodium would be to prepare a large quantity of the purest sodic chloride and crystallize it in a large number of fractions. If then, on analyzing each of these fractions, and determining with the utmost possible accuracy the percentages of sodium and chlorine present, the fractions turned out to be identical, the case would be a very strong one. Something amounting to the same thing has been done; and the results thus far show no reason for believing that sodium contains more than one kind of matter.

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* See Venable. *The Periodic Law* (Chemical Publishing Co., Easton, Pa.), pp. 49, 50.

Sodium, then, represents a perfectly definite and well-defined substance, which we have no trouble in producing at any time, and which has one particularly distinguishing mark (its spectrum) by which it is always characterized. Moreover, it will always be so as long as the present order of nature continues. We may sometimes find that it is not simple, but we shall always be able to obtain it as we do now. Its chloride will always be "salt," and we shall make soap from its hydroxide.

We have spent considerable time upon this matter for the sake of clearness at the outset of our study of the elements. In dealing with subsequent groups, the same amount of detail will not be necessary, unless some of them offer points of peculiar interest.

LABORATORY WORK.

Take 5 grams of sodic sulphate (anhydrous). Dissolve it in the smallest possible amount of water, and add to it dilute sulphuric acid in such quantity that for every molecule of sodic sulphate in solution, there shall be a molecule of hydrogen sulphate (H_2SO_4). Boil down the solution *not to dryness*, but until, on cooling the dish by setting it into cold water, and stirring, crystals separate. It can usually be seen when this point has been reached by taking out a drop on a glass rod, and allowing it to cool, noticing whether as it cools it crystallizes. Drain off the water from the crystals as completely as possible; place them upon several thicknesses of filter paper; put some more of the same filter paper over them, and press them strongly until the crystals are thoroughly dry, and no longer dampen fresh filter paper. Compare these crystals with crystallized sodic sulphate with respect to the following points: behavior on heating; effect upon litmus paper when in water solution; behavior when allowed to stand on a piece of filter paper over night.

Weigh carefully about two grams of the crystals. Dissolve them in water. Add from a graduated vessel sodic hydroxide solution until the solution is just neutral to litmus. What weight of actual sodic hydroxide have you added? Evaporate your neutral solution to dryness carefully. Satisfy yourself that the residue is sodic sulphate. What reasons can you see for thinking it is sodic sulphate? What does it mean, according to the dissociation idea, when a solution reacts acid? What, then, is true of this substance in water solution? What are its ions? Can you now form any idea as to what kind of a substance this salt you have made may be? What, then, is probably the reaction when the water solution of the salt is neutralized with sodic hydroxide as above? According to this reaction how much sodic hydroxide would be needed for the quantity of substance you dissolved? Compare the calculated quantity with that actually obtained in your experiment.

Make a *saturated* solution of anhydrous sodic carbonate in water (the solution should be saturated at its boiling-point and then cooled under the faucet, shaken thoroughly, and filtered). Pass a current of carbonic dioxide into the solution for some time, until a crystalline precipitate has separated out abundantly. Drain off the liquid from the crystals, and press them dry with filter paper. (Since the process is somewhat slow, the following experiments may be made while it is going on, using some of the same material furnished by the teacher.)

The substance contains no crystal water. Compare it with anhydrous sodic carbonate as to its behavior on heating (is anything given off in either case?); solubility in water (simply ascertain as quickly as possible which dissolves the more readily); action upon litmus when in water solution; volume of carbonic dioxide given off by a given weight of each of the substances when acted upon by dilute hydrochloric acid. What appears to be the difference between this new substance and the sodic carbonate with which we started? Have you any idea as to its possible constitution? What facts lead you to this theory? Does it explain the behavior of the substance when heated? Express by reactions the formation of the substance (by the process you employed in preparing it) and its decomposition when heated.

LECTURE 36.

NITROGEN; AMMONIA; NITRIC ACID.

WE have now studied quite carefully one of the metallic elements and some of its compounds. We have also seen how closely its peculiarities are imitated by several other elements; and this has led us to study them as a group, as well as separately. We now turn our attention to another element, which is an excellent representative of the non-metallic elements; and it shall be our task to study its behavior carefully, and see how it differs from that of the metallic elements we have just been considering. Finally, we shall study it in connection with some other non-metallic elements which are as closely and strikingly related to it as lithium, cæsium, and rubidium are to sodium.

The element in question is nitrogen: the symbol of its atom is N; and its atomic weight is very closely 14. It is a colorless, odorless gas except at very low temperatures. When cooled to — 146° under a pressure of 35 atmospheres, it condenses like steam to a colorless liquid, boiling at — 193°, and solidifying at — 214° to a snow-like crystalline mass.

We have seen that when phosphorus is burned in a confined portion of air, there remains, after the burning is finished, a gas constituting about four fifths of the original bulk of air taken, and incapable of taking any part in ordinary burning. There was, however, no reason for concluding offhand that this gas was composed of one substance only, and there is no simple method of experimenting which would have enabled us to settle this matter decisively. It is, however, possible, with suitable apparatus, to investigate the question as to whether we are dealing with a single gaseous substance, or a mixture of two or more gases. We found no difficulty in deciding that air was a mixture; and we were able to remove the oxygen by burning phosphorus. The same principle can often be applied in other gas mixtures; that is, we can find some substance which will absorb one constituent and leave the other. In the present case, it happens that the element nitrogen, as obtained from its compounds, unites with metallic magnesium at a red heat. When the gaseous residue left from burning phosphorus in the air is passed over red-hot metallic magnesium, *it is not all absorbed*, as it would be if it were pure nitrogen, but there remains a very small volume of a gas which is not absorbed by any amount of heating with magnesium. The quantity is very small, but the same result is obtained every time. This gas is heavier than nitrogen, and differs from it very markedly in its behavior. On the other hand, all samples of nitrogen obtained *direct from its compounds* are completely absorbed by hot magnesium. It follows, then, that the gas remaining after the oxygen is removed from air is a mixture of *at least* two gases. One is nitrogen, and this constitutes by far the greater portion. The other, present only to the extent of about 1.2 per cent, has been named *argon*. Up to 1894 purified and dried air was thought to contain nothing but oxygen and nitrogen. Lord Rayleigh, while making some very careful determinations of the density of nitrogen, noticed that the nitrogen he obtained from the air was always slightly heavier than that obtained from compounds of nitrogen, and this observation first led to the suspicion that the nitrogen in the air was accompanied by a small amount of a heavier gas.*

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* See Ramsay's *The Gases of the Atmosphere* (Macmillan & Co.), p. 146 *et seq*; also numerous articles and notes in the *Chemical News* from the beginning of 1894 to the present time.

There are other methods by which gas mixtures may be analyzed, but they are, as a rule, more difficult and less satisfactory than the one described above. For example, light gases pass through porous earthenware walls faster than heavy ones do. If a gas is a mixture, the gases composing the mixture will, in general, have different densities; and if this mixture be passed through a long porous tube, the gas which emerges at the other end will be different from what it was when it entered, because a considerable part of the light constituents will have passed out through the walls of the tube. It is a sort of sifting process. Its application is, however, very difficult. All the known methods for dealing with gas mixtures are being very carefully studied just now; and the air is being studied with much more care than has been previously put upon it. This *may* result in the discovery that it is more complex than we now think it is; but for our present purposes we can deal with the air as simply a mixture of oxygen and nitrogen.

That it is actually a mixture and not a compound, is sufficiently clear from the following facts:

1. Its composition is not absolutely invariable; the percentages of oxygen and nitrogen change slightly with circumstances. If it were a compound this would not be so.

2. When passed through a porous tube, the air which emerges contains less nitrogen than the original gas. A *compound* of oxygen and nitrogen would prove to be homogeneous.

3. When air dissolves in water, the oxygen and nitrogen dissolve in different proportions from those in which they exist in ordinary air. Air which has been expelled from solution in water by boiling or otherwise, contains about 1.87 volumes nitrogen to one volume oxygen, instead of 4 volumes nitrogen to one of oxygen. Oxygen is known to be more soluble in water than nitrogen, and it follows that the two gases as present in air, dissolve quite indepen-

dently of one another, which would not be the case with a compound.

4. A mixture of one volume of oxygen with four volumes of nitrogen is identical in all respects with common air; and when the two gases are mixed there is no temperature change, volume change, or any other indication of chemical action.

While, however, it is true that the composition of the air shows variations decided enough to indicate that it is not a chemical compound, it is nevertheless true that the proportions of oxygen and nitrogen are practically constant, and have been ever since the question was first attacked. Oxygen is constantly breathed in by all forms of animal and vegetable life, and used in all forms of combustion as well is in many processes of fermentation or decay; but, on the other hand, it is constantly being restored to the air again. All breathing animals take in oxygen and breathe out carbonic dioxide. When wood, coal, or any animal or vegetable substance burns, carbonic dioxide is one of the products. But plants and trees subsist largely upon carbonic dioxide. They decompose it, and the nature of the decomposition is such that the carbon is utilized by the plant and the oxygen is returned to the air. There are other less conspicuous processes going on by which oxygen is returned to the air, and everything seems to indicate that the income and outgo balance each other very closely. Nitrogen is utilized both directly and indirectly * by plants. It is not directly utilized by animals, so far as is known, although nitrogen compounds are essential food for both plants and animals. Many forms of decay, which is the common lot of all living organisms, result in the return to the air in the free state of some of the nitrogen which they contain. Here again we appear to have a pretty close balance between income and outgo; so that the proportionate quantities of nitrogen and oxygen remain practically the same.

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* For some excellent literature upon this point, see *Year-Book of the U. S. Dept. of Agriculture* for 1895, pp. 69–102; particularly pp. 73–83.

Returning now to nitrogen itself, its most remarkable characteristic is the great stability of its molecule, which we know to consist of two atoms.* The result is that it is very difficult to cause it to unite directly with any other element. Magnesium unites with it at a red heat, as we have seen; and when a mixture of nitrogen and oxygen is exposed to the action of a series of strong sparks from an induction coil, the two gradually unite. The product formed is an oxide of nitrogen which dissolves in water, forming an acid; and if the sparking be conducted in presence of some alkali, like sodic hydroxide, all the nitrogen can be made to unite with oxygen. This is, in fact, another method by which argon can be obtained from the air, namely, by introducing into a confined volume of air some extra oxygen, and sparking over alkali with a powerful coil, until no further change of volume takes place. The remaining oxygen can then be absorbed by phosphorus, or by some other means, and the argon, which is not affected by the above treatment, is left behind.

But although it is so difficult to make compounds of nitrogen directly, it is at the same time true that it forms a large number of exceedingly important and stable compounds, some of which are widely distributed in nature, as well as useful for many purposes. The most marked examples are the salts of nitric acid, or the *nitrates*, and *ammonia*, which is a compound of hydrogen and nitrogen. For our supply of these compounds, we are indebted to the wonderful processes of growth and decay on the part of animal and vegetable organisms, past and present.

Nitrogen in some form is essential to the growth of plants or animals; and all plants and animals contain large quantities of it in the form of very complex compounds. Plants take their nitrogen, mainly at least, from the soil, where it exists in the form of nitrates (principally of sodium and potassium), which have been formed in the soil by the action upon decaying vegetable and animal matter of small organisms called "ferments." Animals take their nitrogen mainly from the animal or vegetable food they consume. The enormous natural deposits of nitrates, such as the sodium nitrate beds of Peru and Chile, are very probably due to the slow decay of marine animal and vegetable matter, in contact with calcic and sodic carbonates, the whole region having been originally covered by the ocean, and finally raised above the surface by some movement of the earth's crust.*

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* See pp. 105–106.

These deposits are, for us, great reservoirs of nitrogen compounds. On the other hand, we find our main supply of ammonia and its compounds among the products obtained by heating soft or bituminous coal, which is the remnant of the forests of past geological ages. The heating of bituminous coal out of contact with air is carried out on an enormous scale in the manufacture of coal-gas for illuminating and heating. A number of nitrogen compounds are obtained as by-products, and most of them are very important commercially. One of the most important, and the only one to be considered here, is *ammonia.*

This substance is formed whenever animal matter (which consists mainly of compounds of carbon, hydrogen, oxygen and nitrogen) decays in the air. The overpowering, suffocating odor of decaying fish or offal is due largely to the ammonia which is being evolved. It is also obtained when such substances are heated to a high temperature out of contact with the air.

Neither of these methods is a convenient one for obtaining ammonia in the laboratory. It is best obtained by heating some one of its numerous compounds with slaked lime (calcic hydroxide). Other methods will come to light as we go on with our study.

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* *Year-Book U. S. Dept. of Agriculture,* 1895, p. 85.

LABORATORY WORK.

1. Place in a test-tube a dry mixture of about half a thimbleful of gelatine with about twice its bulk of "soda-lime" (a mixture of sodic hydroxide and lime).

Heat the mixture gently. Note the odor of the escaping gas, its action upon moist litmus paper, and its behavior when a glass rod moistened with strong hydrochloric acid is held near the mouth of the tube. (Instead of gelatine, horn, glue, or leather in very small fragments may be employed.)

2. Mix in a test-tube about a gram of ammonic chloride with its own bulk of dry slaked lime. Heat the mixture gently over the flame; examine the gas in the same manner as in the last experiment.

3. Again gently heat the tube with its contents for a minute, partially closing the mouth of the tube by the thumb; then close it completely, and invert it mouth downward in a beaker of water. Remove the thumb. Explain what happens.

4. Fit up a test-tube with perforated cork and delivery-tube. Place in it about four times as much of the mixture of ammonic chloride and slaked lime as you had before. Support the test-tube in such a position that it can be heated by the Bunsen lamp, and so that its delivery-tube nearly reaches the surface of the water in a second test-tube, which should be about half filled with *distilled* water. Gently heat the first test-tube with its contents for a few minutes, and note the behavior of the gas as it passes into the water; then remove the second test-tube and stop heating. Note the odor of the water in the second test-tube, and try its action upon litmus paper. Pour half of it into a clean test-tube, and boil it for a few minutes. Note the odor accompanying the escaping steam. Notice also that of the water remaining after several minutes' boiling. What facts are brought out by your experiments up to this point? Does the reaction with litmus paper give you any information as to any of the ions present in the solution? What, then, appears to be the nature of this solution?

For the following experiments a solution exactly similar to the one you have just prepared will be furnished you. To about 10 c.c. of it add dilute hydrochloric acid until you obtain a neutral solution. Evaporate the neutralized solution to small bulk and cool it. Take some of the crystals and heat them on a porcelain cover. What becomes of them? Carefully heat some in the bottom of a test-tube. Take some more and heat them with slaked lime in a test-tube. Result? Take some more; dissolve them in water, and test for the ion of hydrochloric acid. Sum up in your notes the results you have reached by your experiments. What do these facts seem to you to indicate? Be careful to keep strictly within the limits of your own observations, and be content to leave the matter just where your experiments leave it. State no conclusions except such as are genuine ones.

We can easily obtain gaseous ammonia by gently heating its water solution. In the following experiments, which will give you some insight into the composition of the gas, we will obtain it as just described.

5. Fill a ⅛-inch test-tube with chlorine; close it with the thumb or with a cork and bring it mouth downward into a strong solution of ammonia contained in an evaporating dish or small crystallizing dish. Remove the thumb. When the action is over, close the tube; transfer it to the pneumatic trough and allow the ammonia solution in the tube to be replaced by water. Finally, close the tube again, remove it from the water; turn it over, and satisfy yourself that the gas left in the tube has the ordinary characteristics of nitrogen. If necessary for thorough work, collect another test-tube full of chlorine and repeat the experiment.

6. For the next experiment students may work in pairs.

Set up the apparatus shown in Fig. 42. *A* is a 100 c.c. flask, partially filled with strong ammonia; *B* is a U tube containing small lumps of lime to serve as a dryer; *C* is a piece of hard glass tubing about ¼ inch internal diameter; *D* a small delivery-tube dipping under dilute sulphuric acid; *E* a test-tube filled with the same acid. Tube *C* should be about five inches long. Into the middle portion of it push a tight roll of copper gauze about two inches long. The joints at the ends of *C* are sleeve joints.

Heat the small flask gently. Ammonia will come off rapidly, and in a minute or two all air will be swept out of the apparatus; then heat the middle portion of *C* with a good Bunsen flame as hot as possible, regulating the heating of *A* at the same time so that the current of gas is rather slow, just rapid enough, in fact, to keep the water from backing up tube *D*. Allow the apparatus to run until a sufficient quantity of gas has collected; then remove tube *D* from the water *at once*. Close *E* with the thumb, remove it from the dish; turn it over and bring a lighted match near the mouth.

7. Take the little tube formerly used in determining the volume composition of hydrogen chloride (see p. 97). Place in the bent portion about 2 grams cupric oxide in lumps about the size of a shot. Fill the tube with dry ammonia gas by bringing it mouth downward over a vertical piece of tubing projecting upward from the second limb of the U tube *B* (Fig. 42). This vertical tube should pass well up into the little bent tube. When the current has run for a few minutes, slowly remove the tube and *at once* close the pinch-cock. Heat the cupric oxide over a flame as long as any action takes place. Remembering the results of your last experiment, what appears to be formed in the tube? Cool the tube and open it with its mouth under water. What is the residual gas?

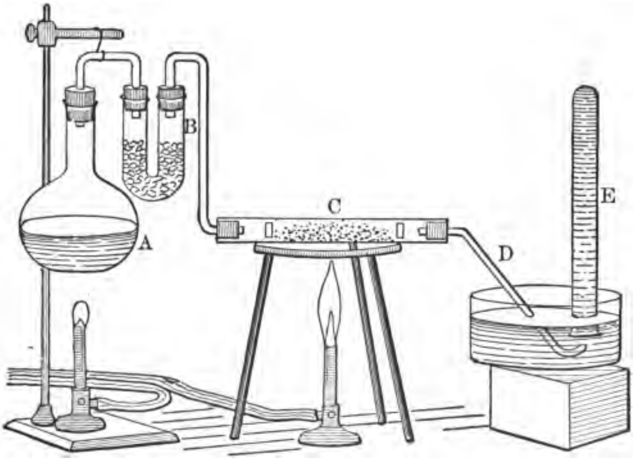

Fig. 42.

VOLUME CONSTITUTION OF AMMONIA GAS.

Fill a test-tube with chlorine * by collecting the gas over a strong salt solution. Close the mouth of the tube with the thumb; place it mouth downward in an evaporating dish nearly full of strong ammonia; remove the thumb. What takes place? Transfer the tube to a trough of water and allow the ammonia solution to be replaced by water. Mark by a rubber band the height at which the water-level in the tube stands. We have seen that the residual gas has the ordinary properties of nitrogen (see 5 above). It is known that in this reaction the hydrogen of the ammonia unites with the chlorine, the nitrogen being set free.

Now, in what volume proportions do hydrogen and chlorine unite? How much chlorine did you have? How much hydrogen must it have taken, then? How much nitrogen do you obtain? What, then, is the ratio between the volumes of hydrogen and nitrogen which go to make up ammonia? What, then, is the ratio between the number of nitrogen hydrogen atoms in the ammonia molecule?

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* See p. 130.

LECTURE 37.

AMMONIA AND ITS COMPOUNDS. NITRIC ACID.

AMMONIA gas is about $\frac{6}{10}$ as heavy as air (0.589) and 8.5 times as heavy as hydrogen. One litre of it at 0° and 760 mm. weighs 0.7635 of a gram. We have begun the study of its composition in the laboratory, and we will now look at the results of other experiments bearing upon the same point. The following are particularly significant:

1. When ammonia gas is subjected to the action of sparks from an induction coil, it is completely transformed *without loss of weight* into a mixture of nitrogen and hydrogen, and the same thing takes place when it is passed through a red-hot tube.

2. When ammonia gas is passed over heated cupric oxide, water is formed, and a gas passes on, which, when collected and examined, proves to be nitrogen.

3. When a water solution of the gas is subjected to the action of the electric current, gases appear at the two electrodes; and these, when collected and examined, prove to be nitrogen and hydrogen. In this case, as in that of water, we add to the solution a small quantity of another substance, in this case ammonic sulphate. (It will be remembered that in case of water we added sulphuric acid.) In both cases we find that no matter how long the current runs, the quantity of the substance we add is unchanged; and we therefore conclude that it must play some intermediate part, and that it is the water in one case, and the ammonia in the other from which the two gases collected come.

The facts stated above admit of only one interpretation: ammonia must contain nitrogen and hydrogen, and nothing else.

As to its composition by volume, the following facts are of assistance:

1. When a solution of the gas is electrolyzed, the volumes of nitrogen and hydrogen obtained are to each other as *one to three.*

2. When dry ammonia gas is separated into nitrogen and hydrogen by the action of electric sparks, the volume increases during the process and finally becomes just double the volume of ammonia taken, after which no more volume change takes place. To analyze the resulting mixture of gases, it is only necessary to pass a definite volume of it over red-hot cupric oxide, when the hydrogen forms water with the oxygen of the cupric oxide. The nitrogen remains unaffected, and is found to be one fourth the total volume of gas analyzed; which means that the volumes of nitrogen and hydrogen present are in the proportion of one to three. (See also your own laboratory results.)

From these facts it follows that there are three times as many hydrogen as nitrogen atoms in the molecule of ammonia; but we do not yet know whether the formula is NH_3, or N_2H_6, or N_3H_9. If, however, we can get at the weight of its molecule we can settle the question. We have seen that ammonia is 8.5 times as heavy as hydrogen. That means that its molecule is 8.5 times as heavy as the hydrogen molecule and 17 times as heavy as the hydrogen atom; that is, its molecular weight is 17, and since the atomic weight of nitrogen is 14, it follows that the formula of the ammonia molecule is NH_3.

Ammonia gas may be liquefied with comparative ease; and this fact is of considerable practical importance. Since this is the first time we have come across a gas which is really important in its liquefied form, we will take the opportunity to look at some of the most important facts connected with liquefaction of gases generally.

1. Any gas may be liquefied at the ordinary pressure by cooling it to a sufficiently low temperature.

2. Some gases may be liquefied at the ordinary temperature by simple compression. Experiment shows that every gas has what is called its *critical temperature*, above which no amount of pressure will reduce it to a liquid. If, however, the temperature be below the critical point, then a sufficient pressure will liquefy the gas. Now the critical point for ammonia gas is at 130°, and it follows that the gas may be liquefied by pressure at ordinary temperatures. It only requires a pressure of about 7 atmospheres (105 lbs. per square inch), and it is a comparatively easy matter to apply this pressure. In practice it is accomplished by large steam force-pumps, which compress the gas into specially constructed cylinders, where it is liquefied. The liquid ammonia rapidly evaporates when the pressure is removed, and in doing so absorbs much heat. Accordingly the liquid ammonia is used to cool the air of "cold-storage" rooms in meat-packing establishments.

For this purpose the liquid is sometimes caused to circulate through pipes just as steam is distributed for heating purposes. The gas which is formed by the evaporation of the liquid comes back to the pump and is again liquefied, and so on. Another way of using the liquid is to pass it through pipes immersed in a strong salt brine, which is thus cooled nearly to its freezing-point (— 21°). The cold brine is then pumped through a system of pipes surrounding the walls of the storeroom, and finally back to the tank, where it is cooled down again.

Ammonia is commonly used in water solution under the names of *ammonia water*, *aqua ammonia*, or sometimes *spirits of hartshorn*. It is used in cleaning, and behaves something as other alkaline solutions do, though not to the same extent.

It has some medicinal uses, and is an important reagent in the laboratory.

As we have seen, it is strongly alkaline, and when neutralized by acids gives salt-like bodies. Altogether its behavior reminds us strongly of that of the hydroxides of sodium and potassium.

The salt obtained by neutralizing it with hydrochloric acid is called ammonic chloride, and proves, on analysis, to have the formula NH_4Cl. Under certain conditions it crystallizes in cubes as sodic chloride does. When ammonia is neutralized with nitric acid, crystals are obtained which are similar in shape to those of potassic nitrate, and when it is neutralized with sulphuric acid, the resulting salt forms crystals similar in shape to those of potassic sulphate.

On the basis of such facts, Ampère, in the early part of the present century (1816), advanced the view that these salts should be regarded as the salts of a hypothetical group NH_4; and this involves the solution of ammonia in water being regarded as the hydroxide of this same hypothetical group. This view is to-day held universally. It is true that the group itself has never been isolated, but it must in fairness be said that there is some indication that a mercury solution, or *amalgam* of it, has been formed. When a little sodium amalgam is dropped into a solution of ammonic chloride a very decided action takes place. The most marked feature of it is the swelling of the mercury into a frothy mass, which occupies about twenty times the bulk of the original mercury. As the frothy mass increases in bulk it gives off bubbles of gas. It is easy to see that one of these gases is ammonia, for the gas turns moist red litmus blue, and there is, moreover, the evidence of the odor. The other gas is inflammable, as can be seen, and proves on closer examination to be hydrogen. Still further, the gases are evolved in the proportion of 2 volumes ammonia and 1 volume hydrogen; and this is the proportion in which they should be evolved if they resulted from the decomposition of NH_4 into ammonia and hydrogen. The reaction would be

$$2NH_4 = 2NH_3 + H_2.$$

That is, twice as many ammonia as hydrogen molecules are formed, and they will consequently occupy twice the gaseous space. Taken all in all, the facts are decidedly interesting, and must be given some weight in considering the reasons for adopting the foregoing view as to the compounds which ammonia forms with the acids. The group NH_4 is called *ammonium*, and behaves just like a metal with a replacing power of *one*. The salts are named accordingly. The hydrochloric acid salt is *ammonic chloride*; the nitric acid salt, *ammonic nitrate*; and the sulphuric acid salt, *ammonic sulphate*. The solution of ammonia in water is believed to contain an *ammonic hydroxide* (NH_4OH), and the evidence that this view is correct is to-day very strong.*

The next compound of nitrogen to be considered is nitric acid; but before beginning its study we will consider some points bearing upon the oxygen compounds of the non-metals generally. It will be remembered that the oxides of the non-metals usually form acids when they are brought in contact with water. Bearing in mind how such metallic oxides as sodic oxide or potassic oxide behave, when brought into water, we might well consider it probable that a non-metallic oxide would behave in a similar manner, and that the acid solution obtained, would prove to be a solution of the hydroxide of the non-metal, in the same way that the alkaline solution is the hydroxide of the metal. In a very few cases this appears to be true, but as a rule the acid, when separated from the water solution and analyzed, does not prove to have the formula of an hydroxide at all, but has a formula which is one or two molecules of water short of the hydroxide formula. For example, one of the oxides of nitrogen has the formula N_2O_5, in which the replacing power or *valence* of nitrogen is evidently five.* When this substance is brought in contact with water we might be inclined to predict that the product would be an hydroxide of the formula $N(OH)_5$. As a matter of fact the product is nitric acid, whose analysis shows that it has the formula HNO_3, which represents the above hydroxide *less two molecules of water*. Again, in case of sulphur we have an oxide SO_3, where sulphur has a valence of six. When this is dissolved in water, *sulphuric acid* results, and its formula is certainly H_2SO_4,

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* See Remsen's *Chemistry*, p. 270; also Remsen's *Organic Chemistry*, p. 97.

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* In studying the oxides of the elements we find the following types (X represents an atom of any element): X_2O, XO, X_2O_3, XO_2, X_2O_5, XO_3. Other types are rare. The chlorides run thus:

$$XCl, XCl_2, XCl_3, XCl_4, XCl_5, XCl_6.$$

The phosphates:

X_3PO_4, $X_3(PO_4)_2$, XPO_4. More complex ones are practically unknown.

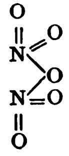
The nitrates:

XNO_3, $X(NO_3)_2$, $X(NO_3)_3$. More complex ones are practically unknown.

The sulphates:

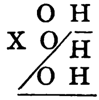
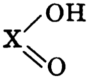
X_2SO_4, XSO_4, $X_2(SO_4)_3$. More complex ones are practically unknown.

We cannot explain these facts even partially, and we can at present form no idea how the same element can, under different circumstances, unite with oxygen or some other element in two different proportions. In order, however, to help us use the facts, we sometimes think of the holding or replacing power of an element as if it were measured by lines of force or *bonds* extending out from the atom. For example, the formula of water can be written $\begin{matrix}H\diagdown\\H\diagup\end{matrix}\!O$ and viewed as though the oxygen atom possessed two such bonds and each hydrogen one. The oxide of nitrogen N_2O_5, mentioned above can be written thus:



as though each nitrogen atom had five bonds and the oxygen two. The idea is, however, of only occasional service, and is only the rudest kind of an attempt to represent facts. It is best kept considerably in the background.

which is two molecules of water short of the formula of the hydroxide $S(OH)_6$. These are only two out of many cases which go to show us that no elementary atom finds it easy to carry many hydroxyl groups attached to it.

In cases where we should expect to get such compounds, that is, hydroxides containing several hydroxyl groups, we generally obtain instead a compound which is a sort of tumble-down ruin of the expected hydroxide. What appears to take place in such cases is that from two hydroxyl groups a water molecule forms and separates from the molecule thus:  $X\begin{matrix}O\,H\\ O\,H\\ O\,H\end{matrix}$ leaving an oxygen atom attached to the element in question where there were formerly two hydroxyl groups attached; thus the compound resulting in the case just given might be  $X\begin{matrix}OH\\ O\end{matrix}$ or $XO(OH)$. This process is called the "splitting out" or "splitting off" of water from the molecule, and it is something that is not infrequently met with in compounds containing hydroxyl groups: indeed it may happen several times in the same molecule. Most of the acids containing oxygen appear to be just such "ruins," and it will help us understand many things about them if we keep this in mind. Something of the same kind happens also in case of the hydroxides of the metals, particularly in cases where there are several hydroxyl groups present: and we have as resulting products intermediate compounds, in which both oxygen and hydroxyl are bound to the same element.

Returning now to nitric acid, it can be made by a method which has already been mentioned as almost universally applicable to the preparation of volatile acids, namely by distilling some suitable salt of the acid in question with sulphuric acid. The temperature should be just high enough to cause the resulting acid to distil over.*

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* See p. 197.

The best salt to use when the acid is made on the large scale is sodic nitrate, on account of its cheapness; in the laboratory, potassic nitrate is more convenient

LABORATORY WORK.

PART I.

In a small retort, place 30 grams potassic nitrate (roughly weighed) and about 20 c.c. of concentrated sulphuric acid. Pass the neck of the retort into a clean, dry flask * of about 150 c.c. capacity, which is to serve as a receiver for the acid which distils over. Arrange the apparatus so that a slow stream of cold water can be kept running over the receiver during the process, to cool and condense the acid vapors. If this is not convenient, arrange so that the receiver is partially immersed in cold water contained in the pneumatic trough. A small piece of cloth laid over the receiver with its edges dipping in the water is a good addition. See that the whole apparatus is set up in a thoroughly neat manner.

Heat the retort with a low and carefully regulated flame. During the first part of the heating the lamp should be held in the hand constantly. The contents of the retort will soon liquefy and the nitric acid will begin to distil over. Continue the heating until about 18 c.c. have collected in the receiver. Then detach the retort and allow it to cool until the hand can just be borne on it. Pour out a little of the residue into an evaporating dish and set it aside to crystallize. Throw the rest away, washing it down the sink with plenty of water. When the portion set aside has crystallized, satisfy yourself that the crystals are potassic sulphate. Set the receiver containing the acid aside for future experiments, *but do not cork it;* instead, place over the neck of the flask an inverted beaker, which must be of such size as to fit down over it loosely, the inner bottom of the beaker being in contact with the rim of the flask.

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* To dry a flask, heat it carefully and uniformly over a *smoky flame* until the bulb is rather too hot to be handled comfortably; then either blow a rapid current of air through it by inserting through the neck a tube connected with the bellows of the blast-lamp; or else draw air through by the suction-pump.

PART II.

NITRIC ACID.

Note and record the color and appearance of the acid collected during the last exercise. (1) Put a little in a test-tube (about 5 c.c.) and boil it. Note what takes place. *Save this acid.* (2) Take about the same amount of the original acid and pass a current of carbonic dioxide through it for some time. Note what happens. *Save the acid.* (3) Measure out just 5 c.c. of the original acid into a dry test-tube. Rinse it carefully into an evaporating dish or a beaker; add a little litmus solution, and neutralize with the sodic hydroxide solution, of which you know the strength, carefully noting and recording the volume used.

Next measure out 3 c.c. of the acid saved from (1): rinse it into an evaporating dish, and neutralize it with the sodic hydroxide solution. Finally do the same with the acid saved from (2). Calculate how much hydrogen nitrate (or "real nitric acid") is contained in one c.c. of the acid as originally prepared, in one c.c. of the acid after it has been boiled, and in one c.c. of the acid through which carbonic dioxide has been passed.

Sum up carefully and systematically in your notes the facts at which you have arrived. What conclusions do they suggest? Restrict yourself here, as always, to such conclusions as seem to follow directly from your experiments.

PART III.

Try the action of nitric acid * upon the following metals: zinc, copper, lead, mercury. Use about ⅛ of a test-tubeful of acid each time, and about a gram of the metal, as nearly as you can estimate it. In each case see first if there appears to be any action in the cold: then apply heat. Work as rapidly as you can. Watch the materials carefully during the actions and keep full notes. *Set aside the tubes with their contents.* What differences do you notice between the action of this acid upon, say, zinc, and the action of hydrochloric or sulphuric acid upon zinc? Is there any evidence that a gas is given off? What is the evidence? Is the gas hydrogen? Take a 250-c.c. flask provided with cork and delivery-tube neatly and tightly fitted. Put into the flask about 10 grams copper, and cover it with dilute nitric acid like that just used. Mount the flask in proper position and begin collecting the gas in a test-tube. What is the color of the gas in the flask? What color is it in the test-tube? Allow the test-tube to fill up with the gas: lift it out of the water. What happens? Fill another test-tube about one third full of the gas. Carefully tilt the test-tube to one side until one edge of the rim just leaves the water and a single bubble of air passes up through the water and mingles with the enclosed gas. (Place a piece of white paper behind the test-tube during this experiment.) What happens? Is this effect due to the oxygen of the air or the nitrogen? Of course the most direct method of settling this question would be to try both, and if time permits or if oxygen and nitrogen are both available,* it will be best to do so; but there is another way of getting at it. If we confine some of the gas over water, and then allow air to enter, one bubble at a time, by inclining the tube, as above, we can by working carefully, see that the effect noted diminishes constantly, and that finally there is no effect. Now, there evidently remains standing over the water *whichever of the two gases of the air was not used in the process.* (How do your previous experiments indicate that this will be the case?) Which of the gases of the air is this gas that is left, or, rather, which does it appear to be under ordinary tests? Sum up your results in as concise and pointed form as possible.

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* For this work the strong nitric acid of the laboratory should be diluted with twice its bulk of water.

Next take one of the test-tubes containing the solutions obtained by acting upon metals with nitric acid. Evaporate a few drops to dryness in an evaporating dish *over steam.* Dissolve the residue in a few drops of water, and test for the nitrate ion.

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* A small quantity of nitrogen is readily obtained by heating gently half a test-tubeful of a mixture of potassic dichromate and ammonic chloride. Reject the first two test-tubefuls collected.

LECTURE 39.

NITRIC ACID; OXIDES OF NITROGEN.

Absolutely pure hydrogen nitrate is a colorless liquid, which begins to boil at 86°, but which cannot be boiled without undergoing some decomposition, the products of which are water, oxides of nitrogen, and oxygen. It continues to decompose as the boiling continues; but finally an equilibrium point is reached and an aqueous nitric acid solution distils over. This solution contains about 68% hydrogen nitrate. It appears, then, that if we boil pure hydrogen nitrate or very concentrated nitric acid, we obtain in the end a rather weaker solution. If, on the other hand, we start with a very weak solution, what comes over at first is mostly water, and the solution grows constantly stronger: finally a mixture of acid and water distils over, which has the same strength as the one we obtained above, i.e., it contains about 68% of acid. We shall see that something similar is encountered in case of hydrochloric and sulphuric acids. Apparently they cannot exist in water solution above a certain concentration, at the temperatures to which they are subjected when their water solutions are boiled. The most conspicuous case we have had is that of carbonic acid, which is only capable of existence in extremely dilute solution even at ordinary temperatures, the result of which is, as we have seen, that whenever carbonic acid is formed in a reaction it breaks down almost entirely into carbonic dioxide and water; but it should be clearly seen that there is only a difference in degree between this case and that of nitric acid. When we made nitric acid we had to heat the retort, and the resulting nitric acid was partially decomposed.

Commercial "concentrated nitric acid," or *aqua fortis*, is a colorless water solution containing about 68% of hydrogen nitrate. It is purified principally by distillation. It undergoes a slight decomposition when exposed to sunlight, becoming yellow and evolving red fumes. It dissolves most metals, forming nitrates.

The most important and fundamental feature of nitric acid, which gives it a large part of it great usefulness is, strangely enough, due to the nature of its *decomposition products*, and the ease with which it decomposes. At the same time it makes the study of the reactions of nitric acid exceedingly difficult; because in almost every reaction the final products which we obtain are not the products of the action of the acid alone, but also of its decomposition products, especially the oxides of nitrogen, and oxygen. About the only exceptions are the simple neutralization reactions. When nitric acid is neutralized by an alkali like NaOH or KOH, all goes smoothly, and the reaction is perfectly regular. When the oxide (see page 132, note) of a metal is acted upon by nitric acid the reaction is regular, and the same is true of its action upon the metallic carbonates; but in practically all other cases we have pretty complicated reactions, many of the most common ones being, to this day, very imperfectly understood.

We have seen that when nitric acid is boiled alone there is, at best, only a partial decomposition; but the case is quite different if there is, in contact with the nitric acid, some substance which is readily acted upon by oxygen. In the former case we may consider that the two opposite reactions of decomposition and recomposition are in equilibrium. In the latter case the introduction of the easily oxidized substance prevents equilibrium being reached, for one of the decomposition products is removed as fast as it is formed. The result is, that the decomposition of the acid and the action of the oxygen upon the substance introduced continue until one or the other is used up. *It is this oxidizing power of nitric acid which is its main feature*, and this tendency, so prominent and ever-present, enters into almost all the reactions in which nitric acid plays a part, and makes them very difficult to analyze.

Take for example the action of nitric acid upon the common metals, such as zinc, iron, lead, copper, and mercury. No one knows to-day precisely what the action is. It appears to vary with the temperature, the strength of the acid, and the nature of the metal. We generally get the nitrate of the metal—that is quite uniformly the case—and we practically always obtain water; but there is always some nitrogen compound obtained also, and this is very variable, even with the same metal. Every considerable change of temperature, or concentration of acid causes it to vary. The fact is that nitric acid heated by itself appears to decompose with great regularity according to the reaction

$$2HNO_3 = H_2O + 2NO_2 + O,$$

but when its decomposition is brought about or aided by the presence of some second substance, it decomposes in different ways according to circumstances. One or more of the *oxides of nitrogen* will generally be among the decomposition products. Of these oxides five are known:

Nitrous oxide, N_2O;
Nitric oxide, NO;
Nitric trioxide, N_2O_3;
Nitric peroxide, NO_2;

and finally

Nitric pentoxide, N_2O_5;

which is the oxide which with water gives nitric acid, and need not be considered among it decomposition products.

In addition to these four oxides we have to consider *free nitrogen* and *ammonia*, which result under certain conditions. The reaction between copper and nitric acid is probably as good an average case as any, and we will consider it for a few minutes.

When this reaction takes place at ordinary temperatures, between copper turnings and a nitric acid of medium strength (such as would be obtained by diluting one volume of strong 68% acid with from one to two volumes of water), the main gaseous product is easily shown to be *nitric oxide* NO, but as the reaction goes on and the acid grows weaker the product varies.*

The reaction is commonly given as follows:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O,$$

and this is known to represent fairly well what takes place under the average conditions specified above; but it is at best only an approximate representation of what really takes place.

Another point—how does it happen that the above products are obtained, and what are the stages of the reaction that finally result in the above products? This question no one can answer at present. Without going far into the matter, there are two ways that suggest themselves of looking at the reaction. It is possible that the reaction starts just as the reactions between zinc and hydrochloric or sulphuric acid do, giving hydrogen thus:

$$3Cu + 6HNO_3 = 3Cu(NO_3)_2 + 3H_2,$$

and that the hydrogen is then oxidized by the nitric acid thus:

$$2HNO_3 + 3H_2 = 2NO + 4H_2O.$$

Combining these two reactions in one we have the reaction given above. The explanation has a certain amount of reasonableness; but on the other hand there is at least one more way of looking at the matter which is just as reasonable, and perhaps a trifle more so.

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* See Newth's *Inorganic Chemistry*, p. 214.

The first action of the acid upon the metal may be an oxidizing action, thus:

$$3Cu + 2HNO_3 = 3CuO + 2NO + H_2O,$$

and the cupric oxide may then be dissolved by the acid, thus:

$$3CuO + 6HNO_3 = 3Cu(NO_3)_2 + 3H_2O.$$

Combining these two we get the same reaction as before. When we have examined the action of nitric acid upon substances other than metals we shall perhaps be in a position to appreciate some evidence bearing upon this point.

It is very easy to attach too much importance to such explanations as these. They are only makeshifts. The whole matter needs more careful study than it has yet received.

The main points to be kept in mind are that nitric acid dissolves most of the metals forming nitrates, and that the other products are water and generally some oxide of nitrogen; nitric oxide, perhaps, as often as any other. It should further be kept in mind that this ready decomposition with oxygen as one of the decomposition products makes nitric acid an exceedingly valuable *oxidizing agent.* We make frequent use of it to bring about the action of oxygen upon substances, especially in solution.

Nitrous Acid (HNO_2) *and the Nitrites.*—Pure nitrous acid is unknown. It only exists in dilute water solution, like carbonic acid. When liberated from its salts by acids, it breaks into water and nitric trioxide, an unstable reddish-brown gas.* Its *salts*, however, are quite stable, and it will be remembered that the same is true of the carbonates. Indeed, the salts of an acid are generally more stable than the acid, and this fact is undoubtedly connected in some way with the tendency of hydroxyl groups to split off as water.

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* From recent experiments it appears probable that this is a mixture of NO and NO_2.

The most common of the nitrites is potassic nitrite, KNO_2. It is usually made by abstracting oxygen from potassic nitrate by heating it with some substance that is oxidized with moderate ease. Metallic lead is usually employed, and the reaction is:

$$KNO_3 + Pb = KNO_2 + PbO.$$

It can also be made by passing nitric trioxide into a solution of potassic hydroxide or carbonate. (Compare this with the making of potassic carbonate by passing carbonic dioxide into potassic hydroxide solution.)

THE OXIDES OF NITROGEN.

These substances have been enumerated above. They are gases at ordinary temperatures.* The most important one is

Nitrous Oxide, N_2O.—It is said to be formed by the action of dilute nitric acid upon zinc, but the most common way of preparing it is to heat ammonic nitrate, which, when gently heated, melts and decomposes with slight effervescence into nitrous oxide and water. The reaction is thus represented:

$$NH_4NO_3 = N_2O + 2H_2O.$$

The heating must be carefully done, for if the temperature be carried too high the decomposition takes place along lines quite different. Nitrogen and nitric oxide are evolved and the experiment is more than likely to terminate in an exceedingly rapid decomposition, or explosion. The reaction in this case appears to be

$$2NH_4NO_3 = N_2 + 2NO + 4H_2O.$$

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* With the exception of N_2O_5, which is a white crystalline solid.

The properties of the gas will be studied in the laboratory. Its most important use is as an anæsthetic. It is used principally by dentists. When it is inhaled in the pure state it produces insensibility. If it be inhaled mixed with air, the effects are different; a kind of intoxication or nervous excitement resulting. This circumstance has given it the name of "laughing-gas."

Nitric Oxide, NO, is usually obtained by acting upon copper with nitric acid of moderate strength. It is a colorless gas, only very slightly soluble in water, and unites readily with oxygen at ordinary temperatures to form

Nitric Peroxide, N_2O_4 *or* NO_2.—This gas is a very interesting substance. It appears reddish at ordinary temperatures. If, however, some of it be enclosed in a suitable vessel and cooled down, a temperature is finally reached at which the gas is colorless. If we reheat it and carry the temperature up, say, to 150° or so, the color grows darker and darker red-brown as the temperature rises, until finally it is almost opaque. If we make a determination of its density, using the colorless gas obtained by cooling it down, we obtain a number close to 46, which corresponds to the molecular weight 92 and the formula N_2O_4. If, however, we take the gas heated above 150°, we find a density of 23, corresponding to the molecular weight 46, and the formula NO_2. At any intervening temperature the molecular weight lies somewhere between the two values. The facts seem to indicate very clearly that we are dealing here with a very beautiful case of an easily reversible reaction:

$$N_2O_4 \rightleftarrows NO_2 + NO_2.$$

At very low temperatures the reaction "from right to left" prevails. Above 150° the reverse reaction prevails. At any temperature between these points both reactions are in operation and *in equilibrium,* and this equilibrium is reached when certain proportions of NO_2 and N_2O_4 have been formed.*

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* It is easy to calculate from the result of a density determination just what per cent of the gas is NO_2 and what per cent is N_2O_4 at any given temperature. As the method involves only a little very simple algebra, and as it applies in a number of cases, it will be given here.

The density of N_2O_4 referred to hydrogen is 46. If it were all dissociated into NO_2 molecules there would evidently be twice as many molecules as before, occupying (according to Avogadro's law) twice as much gaseous space as if there were no dissociation. As a result, a given volume of the gas would contain half as much matter as it would if there were no dissociation. Hence, the density would be 23. If the gas is not all dissociated, the value found for the density will lie somewhere between 46 and 23, depending upon the number of dissociated molecules.

Let A = the density when there is no dissociation;
a = the density as observed;
x = the fraction (decimal) expressing the percentage of dissociated molecules;
n = the number of molecules into which the original molecule dissociates.

Suppose there are 100 N_2O_4 molecules to begin with. Let $100x$ dissociate. How many molecules are there in all now? Each molecule that dissociates splits into n new ones, and since $100x$ have dissociated, there are $100nx$ NO_2 molecules formed, while $100 - 100x$ are left undissociated. The total number of molecules present is, of course, the sum of the undissociated and the dissociated, so there has been an increase from 100 to $100nx + (100 - 100x)$, or $100(1 + (n - 1)x)$. *Since the density decreases as the number of molecules increases, we have*

$$100 : 100(1 + (n - 1)x :: a : A,$$

or

$$1 : 1 + (n - 1)x :: a : A.$$
$$(n - 1)ax = A - a;$$
$$x = \frac{A - a}{(n - 1)a}.$$

In the present case $A = 46$.

Let us suppose that $a = 30$.

Since each molecule splits into two, $n = 2$, and we have

$$x = \frac{46 - 30}{30} = 0.533, \text{ or the gas is } 53.3\%$$

dissociated. We shall have occasion to refer back to this formula in the future.

Nitric peroxide readily gives up one atom of oxygen to easily-oxidized substances and passes back into nitric oxide.

LABORATORY WORK.

Aside from the method we have already noticed (burning out the oxygen from air), the best methods for preparing nitrogen are:

1. By heating ammonic nitrite, NH_4NO_2 (a salt of nitrous acid). The salt melts and decomposes into nitrogen and water. A mixture of potassic nitrite and ammonic chloride may be employed instead of ammonic nitrite.
2. By passing a mixture of ammonia gas and air over heated cupric oxide.
3. A very simple and easy method is to heat gently in a test-tube, provided with cork and delivery-tube, a mixture of three parts potassic dichromate and one part ammonic chloride, previously pulverized and mixed. The reaction will be more easily understood after some further study, and will not be discussed now. The method is exceedingly easy and satisfactory

The most profitable method for our present purposes will be the second. It is carried out as follows:

A piece of hard-glass tubing about six inches long is filled with coarsely granular cupric oxide. One end is connected by the cork and rubber tube with the 'lithia bottle' *A*, which is full of water. Fig. 43 shows how the connections are made. The flask or bottle *C* contains strong ammonia.

The lithia bottle being full of water, the cupric oxide tube is heated by a Bunsen lamp to dull redness; the pinch-cock *E* is opened a very little and very gentle suction is applied by the lips at the end of the long siphon-tube, which is thus filled with water. The pinch-cock is now regulated so that the water drops from the end of the siphon at the rate of about four drops per second. The effect is to cause a slow current of air to bubble through the bottle *C*. The air carries along considerable ammonia gas with it, and the two pass on together over the hot cupric oxide. Satisfy yourself that nitrogen collects in the bottle *A* as the water recedes. Watch the whole process carefully and see if you can gain any evidence as to other products besides nitrogen. (Try interposing a U tube surrounded by cold water between the tube *B* and the lithia bottle *A*.)

What is probably the action of the ammonia gas upon the cupric oxide? What will this leave in the tube *B*? What now will be the effect of the air upon the contents of *B*? Remember that only nitrogen goes on. In what state would this leave the contents of *B*? Examine the tube *B* while the process is going on and see if its appearance is in accord with your idea.

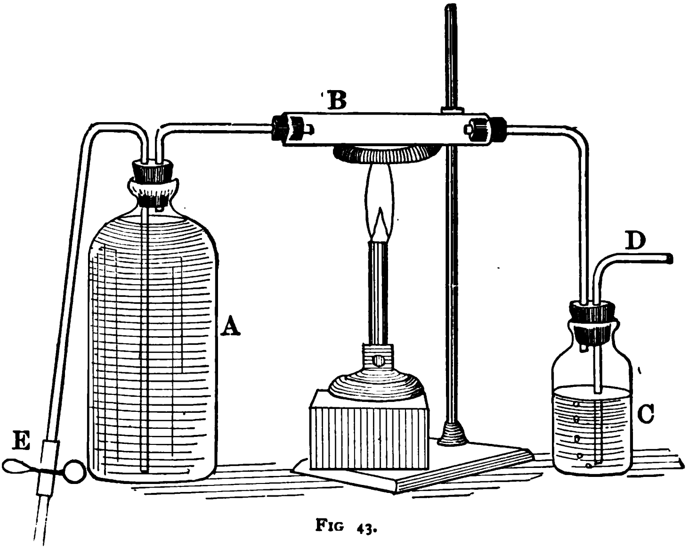

FIG 43.

What is the idea of using, in this process, a mixture of ammonia gas and air? Why would it not be as well in every way to use simply ammonia gas?

OXIDES OF NITROGEN.

Nitric Oxide.—Fit up a 250 c.c. flask with delivery-tube and funnel-tube. Place in the flask about 20 grams copper-turnings and add through the funnel-tube about 50 c.c. of nitric acid, made by mixing the concentrated acid with its own volume of water. The evolution of gas is quite rapid, and it may be necessary to add a little water to moderate the action. Fill several flasks and test-tubes with the gas and let them stand over water until they are needed for use.

We have already partially studied the behavior of nitric oxide (see p. 240). The first question is as to its behavior toward oxidizable substances, and in particular whether such substances as burn readily in the air (a *mixture* of oxygen and nitrogen) will also burn in this gas, which is a *compound* of oxygen and nitrogen.

Open one of the bottles of gas mouth upward and see whether a lighted match or a taper will continue to burn in nitric oxide. Try in the same way a small piece of sulphur (supported upon a little spoon made of a piece of copper wire and a fragment of asbestos paper). Try also a little red phosphorus. In each case see that the burning is well under way before the bottle is opened and the substance introduced.

Try the phosphorus again, and this time plunge the spoon containing it into the gas before it has had time to get well started. Keep full and careful notes of your results.

VOLUME COMPOSITION OF NITRIC OXIDE.

We can decompose nitric oxide by passing it over red-hot copper or iron-turnings. The oxygen attacks the metal, the nitrogen is set free, and can be measured. The following method is more convenient, since it can be carried out at the ordinary temperature. A piece of soft-glass tubing about 8 inches long and ⅛ inch inside diameter is sealed at one end. It is then fitted at the open end with a piece of tightly-fitting rubber tubing about 4 inches long, provided with two pinch-cocks about 2 inches apart. Proceed as follows: Open both pinch-cocks wide and fill the whole apparatus, rubber tube and all, with nitric oxide over water. Close the pinch-cock at the free end of the rubber tube (we will call this pinch-cock No. 1), and turn the whole tube mouth upward. Close pinch-cock No. 2 and open No. 1. Now fill the space between the two pinch-cocks with a ground mixture of iron-filings (or fine turnings) and sulphur.* Shut No. 1;

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* Instead of this mixture a strong solution of sodic or potassic sulphide may be employed, and the action is, on the average, more rapid. The apparatus *must* be tight.

open No. 2, and the mixture will fall into the glass part of the tube. Shake the tube and its contents at intervals for fifteen or twenty minutes: then turn the tube mouth downward and shake the residual iron-sulphur mixture down into the rubber part of the tube. Close No. 2, open No. 1, and fill the rubber part of the tube completely with water. Close with the thumb; place the tube mouth downward in a dish of water, open No. 2, and if the operation has been carefully performed the water will rise rapidly into the tube and fill the space formerly occupied by oxygen. What volume of nitrogen do you obtain? What was the volume of the gas analyzed? What then must be the volume of oxygen? What is the ratio between the volumes of nitrogen and oxygen obtained in the decomposition of nitric oxide? What must be the ratio between the number of atoms of nitrogen and of oxygen in the molecule of nitric oxide?

RELATION BETWEEN NITRIC OXIDE AND NITRIC PEROXIDE.

Fill a test-tube one third full of nitric oxide over water.* Lower the test-tube until water-levels inside and outside are the same, and mark the boundary line between gas and water by a rubber band or by a thread. Fill another test-tube about half full of oxygen. Adjust level and mark the boundary as in the first case.

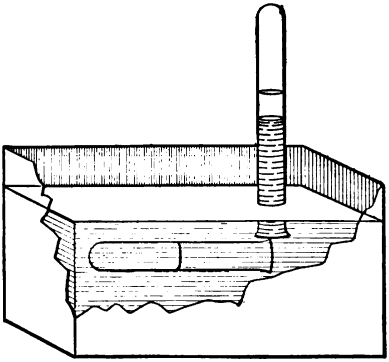

FIG. 44.

Bring the mouth of the nitric oxide test-tube under the mouth of the oxygen-tube (both being, of course, kept with their mouths under water) (see Fig. 44), and incline the nitric-oxide tube until a few cubic centimeters of the gas pass up into the oxygen-tube. The two gases at once combine and form nitric peroxide, which dissolves in the water. Immerse the oxygen-tube fully to cool it; then add a few more cubic centimeters of nitric oxide. Shake the oxygen-tube, keeping its mouth still under water. Mark the levels in the two tubes as when they were first filled. By means of your graduated cylinder or your pipette, measure the volume of the space included between the two threads in case of each tube.

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* Use a small generator which has been freshly charged with copper and nitric acid (1 : 1), and collect the gas as soon as the air is swept out from the flask.

How much nitric oxide have you used? With how much oxygen has it united? What, then, are the proportions by volume in which nitric oxide and oxygen unite to form nitric peroxide? What is the ratio between the number of atoms of nitrogen and of oxygen in nitric peroxide?

REDUCTION OF NITRIC ACID TO AMMONIA.

Into a test-tube put a little granulated zinc and about 5 c.c. dilute sulphuric acid. When hydrogen begins to come off freely, add about 1 c.c. dilute nitric acid, a drop at a time (note carefully what happens when the nitric acid is added). Allow the tube and contents to stand for a few minutes, then pour part of the solution into another test-tube; add sodic hydroxide until the solution is strongly alkaline, and warm over the lamp. Note the odor of ammonia. In what form must the ammonia have been present in the solution before it was made alkaline? What is, then, probably the first action of the hydrogen upon the nitric acid? What next takes place? What happens when the sodic hydroxide is added?

DECOMPOSITION OF NITRATES.

(*a*) Put about 2 grams potassic nitrate into a porcelain crucible. Place the lid so that an opening about ⅛″ wide is left at one side of the crucible, and heat crucible and contents with the full flame of a Bunsen lamp. Cool the crucible. Dissolve the contents with a few drops of water and test with litmus. Dissolve a little potassic nitrate and test that with litmus. Heat some more of the nitrate in a piece of hard-glass tubing. Arrange the apparatus and conduct the experiments as described on page 254.

(*b*) Carefully heat some cupric nitrate in an evaporating dish until the crystal water is driven off. Do not overheat. *The dried substance should be green.* If it blackens, the heat is too strong. Half fill a piece of "arsenic tubing,"* about 4 inches long and sealed at one end, with the dried nitrate (see Fig. 45). By means of a sleeve of rubber tubing adapt a piece of small glass tubing, bent downward so as to pass through one hole of a double-bored stopper in a 6-inch test-tube and reach nearly to the bottom of the test-tube. From the second hole of the stopper comes a straight piece of tubing about 4 inches long. When the whole apparatus is set up, the hard-glass tube should be nearly horizontal, the delivery-tube end being the higher. The test-tube should be about vertical. Support the apparatus by means of a ring-stand and heat carefully with the low flame of a Bunsen lamp, taking care to begin the heating at the front end and work gradually backward as the decomposition proceeds. Note the behavior of the cupric nitrate as the heating goes on, also the appearance of the vertical test-tube. When all the cupric nitrate has been decomposed, rapidly detach the test-tube with its stopper and connections. Close the ends of the connecting tubes with the fingers, and immerse the whole, mouth downward, in the pneumatic trough. Release the connecting tubes and note what happens. Close the mouth of the test-tube by the thumb or by a cork. Have ready the glowing coal of a match. Turn the test-tube right side up; remove the thumb and plunge in the match-coal; finally test the water in the test-tube with litmus.

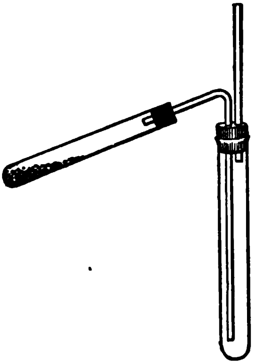

FIG. 45.

Of what does the residue in the hard-glass tube remind you? Examine it carefully. Place a little in a piece of glass-tubing and heat it in a slow current of illuminating-gas (which contains hydrogen).

What can you say of the gases produced on heating the nitrate? Sum up your results now with strict regard to accuracy of statement and keeping well within the bounds of what you have established as *facts.*

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* Hard-glass tubing about ¼″ outside diam.

DETERMINATION OF THE PERCENTAGE OF AMMONIA IN AMMONIC CHLORIDE.

Weigh out accurately about one gram of ammonic chloride on a piece of smooth paper. Carefully transfer it to your boiling-flask and adapt to the outlet-tube a tube about 16 inches long which fits loosely over the outlet-tube. Make a joint by means of a piece of rubber tubing; pass the free end of the long tube through one hole of a *double-bored* cork of size to fit a 100-c.c. flask (see Fig. 46). The flask is to rest on the desk in an inclined position, and the long tube reaches nearly to the bottom of the flask, in which is placed a carefully measured amount (about 10 c.c.) of dilute sulphuric acid whose "strength" is known. Add water until the flask is one third full. Finally support the boiling flask on a ring of the ring-stand with wire netting and asbestos paper; pour into it about 25 c.c. of sodic hydroxide solution. Close with the cork and heat to boiling. What reaction takes place? What becomes of the ammonia? For our present purposes all the ammonia may be regarded as expelled after about fifteen minutes' brisk boiling. Before re-

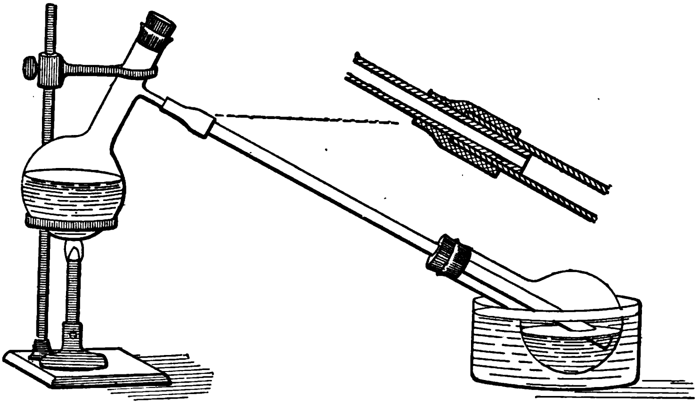

FIG. 46.

moving the lamp take out the stopper from the boiling flask. Next remove the small receiver flask. Add a drop or two of litmus solution and neutralize with sodic hydroxide of which you know the strength.

How much sulphuric acid was there in the 10 c.c. of dilute acid you measured out? How much remains now? What weight of H_2SO_4 has then been neutralized by ammonia? Bearing in mind that ammonia in water solution gives ammonic hydroxide, and that this neutralizes acids just as sodic and potassic hydroxides do, the reaction in this case being

$$2NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O,$$

or, what is the same thing,

$$2NH_3 + 2H_2O + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O,$$

calculate from this latter reaction the quantity of ammonia (NH_3) that has been neutralized. Calculate the per cent of NH_3 in ammonic chloride. Calculate now the percentage of NH_3 in NH_4Cl, using the atomic weights, and see how well your results agree with the calculated percentage.

LECTURE 40.

OTHER ELEMENTS RELATED TO NITROGEN.

We have now made a fairly thorough study of the chemistry of nitrogen. Our main purpose has been to bring out the features which particularly characterize it as a non-metal; and the contrast between it and sodium—one of the best representatives of the metallic elements—is a very sharp one.

We are next to notice that nitrogen, like sodium, presents in its behavior certain peculiarities which are shared by several other elements in a greater or less degree; and that we get our most suggestive and helpful ideas of these elements by studying them as a "group" or "family" of elements.

The other members of the nitrogen family are arranged below in the order of their ascending atomic weights:

Element.	At. Wt	State.	Boiling-pt.	Sp. Gr. (Solid.)
Nitrogen.......	14	Gas.	$-193°$	....
Phosphorus	31	Solid.	290°	1.83
Arsenic........	75	Blackish-gray solid	....	5.76
Antimony......	120	White brittle metallic solid	1200° (?)	6.7
Bismuth	208	White metal with faint reddish tinge	1400° (?)	9.93

On examining the table given above it will be seen that starting with nitrogen, the element of lowest atomic weight, and passing to bismuth with the highest atomic weight, we pass from an element which is decidedly and unequivocally a non-metal to one which shows predominating metallic characteristics, both physically and chemically; and between these two extremes we have elements which manifest decidedly mixed characteristics.

Phosphorus in its chemical behavior shows none of the characteristics of a metal. We shall presently see that in its physical behavior there is a faint suggestion of metallic properties.

Arsenic shows some of the features of a metal. Its color is not unlike the prevailing color of the metallic elements, and its lustre, while not decidedly metallic, is what is called *sub-metallic*, meaning thereby a lustre not quite decided enough to be called really metallic. Chemically, arsenic shows some faint metallic tendencies, but is more closely allied with the non-metallic elements.

Antimony looks metallic, and shows a good deal of metallic behavior in its chemistry.

Bismuth is decidedly metallic, though showing faint traces of non-metallic behavior.

Just now we are mainly interested in the chemical side, so we will take a little survey of some of the chemical characteristics of the different elements and see how these vary with changing atomic weight. Let us first look at the compounds they form with hydrogen:

Element.	**Symbol.**	**Hydrogen Compounds.**				
Nitrogen.......	N	NH_3	N_2H_4	....	N_3H	
Phosphorus	P	PH_3	P_2H_4	P_4H_2	....	
Arsenic........	As	AsH_3	....	....	....	As_2H_2 (?)
Antimony......	Sb	SbH_3	....	....	....	....
Bismuth.......	Bi	....	....	....	....	...

Nitrogen and phosphorus form, as is seen, three compounds each with hydrogen, and the tendency to form such compounds entirely disappears in case of bismuth.

With oxygen they form the following compounds:

Nitrogen.......	N_2O	NO	N_2O_3	$No_2(N_2O_4)$	N_2O_5
Phosphorus....	......	......	P_2O_3	....	P_2O_5
Arsenic........	......	......	As_2O_3	....	As_2O_5
Antimony......	......	......	Sb_2O_3	Sb_2O_4	Sb_2O_5
Bismuth	......	BiO	Bi_2O_3	....	Bi_2O_5

This table of the oxides is of interest principally because it is the character and behavior of the oxides which differ so decidedly in the metals and non-metals.

None of the oxides of nitrogen are basic. Nitrogen has absolutely no power to form salts with the acids. N_2O_3 and N_2O_5 are decidedly acid-forming oxides; that is, when brought into water, in so far as they react with the water at all, they form nitrous and nitric acids respectively. When brought in contact with metallic hydroxides, especially with the soluble ones like NaOH and KOH, they form the sodium or potassium salts of nitrous or nitric acid, according to the oxide reacting.

Phosphorus has no well-defined salt-forming tendencies. When treated with dry chlorine it forms chlorides, two in number, PCl_3 and PCl_5; and these might be regarded as salts of hydrochloric acid; but there is a very clear-cut characteristic of these compounds which serves to distinguish them from the hydrochloric acid salts of the typical metals—*they are unable to exist in water solution.* They are immediately decomposed, and the primary nature of the reaction is this: the chlorine unites with hydrogen to form hydrochloric acid and the corresponding hydroxide of phosphorus is formed. For instance, in case of PCl_3, when this is brought into water, hydrochloric acid appears and the hydroxide $P(OH)_3$ (corresponding to PCl_3) is formed; thus,

$$PCl_3 + 3H_2O = 3HCl + P(OH)_3.$$

It is interesting to notice what a complete reversal this is of what we find so characteristic in case of the metallic elements. Take the case of a metal X forming an hydroxide X $(OH)_3$. The characteristic behavior of this hydroxide toward an acid is

$$X(OH)_3 + 3HCl = 3H_2O + XCl_3;$$

and this is the exact reverse of the reaction given above.

With nitric acid, sulphuric acid, and other acids, phosphorus forms absolutely no salts. Nitric acid simply oxidizes it, as in fact it does most of the non-metals.

On the other hand, both its oxides are acid-formers, and when treated with water yield acids. The acid from P_2O_3 (phosphorous oxide) is called *phosphorous acid*, and its salts are called *phosphites*. That derived from P_2O_5 (phosphoric oxide) is called *phosphoric acid;* and its salts *phosphates*.

Passing on now to arsenic, we find much the same state of things. Arsenic forms one chloride, and this is its sum total of salts forming.

This one chloride, however, is a step in advance of what we found in case of phosphorus, and shows more of the character of a real salt than either of the chlorides of phosphorus. For instance, it can be made by boiling the corresponding oxide with strong hydrochloric acid, which reminds us of the behavior of the metallic oxides, and it can exist in water solution if considerable hydrochloric acid be present. If, however, the pure chloride be brought into pure water, the same thing takes place as we have just noted in case of phosphorus —hydrochloric acid is formed, and an hydroxide of arsenic which shows all the characteristics of an acid:

$$AsCl_3 + 3H_2O = As(OH)_3 + 3HCl.$$

This hydroxide separates as a white precipitate. When treated with sodic hydroxide it dissolves, and on evaporating there is obtained the sodium salt of *arsenious acid*, or *sodic arsenite*.

On the other hand, when this same hydroxide is boiled with concentrated hydrochloric acid, it dissolves and forms $AsCl_3$ again, so this hydroxide shows at once the characteristics of a metallic and of a non-metallic hydroxide.

This reaction we have just noticed is a very interesting one, for it is one of the most striking instances of a reaction that runs in one direction or the other, according to circumstances. As in previous cases we can indicate this as follows,

$$AsCl_3 + 3H_2O \rightleftharpoons As(OH)_3 + 3HCl,$$

and the one circumstance which rules the situation is *the concentration of the hydrochloric acid.* With much water and little hydrochloric acid the reaction runs decidedly from left to right. With little water and much hydrochloric acid the reaction from right to left prevails. If we use intermediate proportions of acid and water both reactions are operative, and the result is that we have the four substances in equilibrium in certain proportions which do not vary so long as conditions remain the same, but which vary with each addition of acid or water.*

* It is usually easy for students to grasp the idea of two opposite processes, one of which undoes the work of the other, but it is not always easy for them to see that when *both of them are operative*, though perhaps at different rates, the result will be only a partial one, and will remain perfectly constant so long as the relative rapidity of the two opposing actions does not change. To help this idea seat itself, consider the case of a fountain. The column of water has a perfectly definite shape, and from a distance appears fixed in magnitude and position, but a nearer view shows it to be a mere mass of rising and falling water, which maintains its shape in virtue of the perfect balance between the rising and falling water. If more pressure be turned on, the column grows in height for a minute, but soon becomes stationary again, and will remain so as long as the pressure is not changed. If the pressure be reduced, the column rapidly diminishes in height, but soon becomes stationary again at a new equilibrium point.

Again: Take a common test-tube and make a hole about $\frac{1}{8}$ inch diame-

Both the oxides of arsenic are acid-formers. Arsenious oxide gives *arsenious acid*, as we have seen. Arsenic oxide As_2O_5 gives *arsenic acid*. Its salts are called *arsenates*.

Antimony forms two chlorides, $SbCl_3$ and $SbCl_5$. $SbCl_3$, antimonious chloride, can be made by dissolving antimony in hydrochloric acid, and also by dissolving the corresponding oxide in hydrochloric acid. It is only partially decomposed by water, a sort of half-way product, called an *oxychloride*, being formed; thus,

$$SbCl_3 + H_2O = 2HCl + SbOCl.$$

There are several of these intermediate compounds, but the one given above is the simplest. This reaction is easily reversible in presence of hydrochloric acid.

Antimony also forms salts with nitric and sulphuric acid. These salts are partially broken down by water, but they are real salts, and are formed by the same reactions as are other metallic salts. They are, however, of no importance, and are very rarely seen.

There is a very curious thing about the chemistry of antimony which is perhaps best approached through the oxy-

ter in the bottom. Clamp it over a sink and slowly run water into it from a faucet. Here, again, we have two opposing actions: the filling action and the emptying action. By regulating the stream from the faucet, it will be found possible to maintain any desired quantity of water in the test-tube. With a certain rapidity of inflow the tube will be half full, and will stay so as long as the faucet is not touched. If a little more water be turned on the tube will fill up a little for a minute and then remain constant at its new equilibrium point, and so on. Every lake maintains its shore-line as the result of a balance between income and outgo. The size of a river is fixed by the ratio between the rate at which water is received and the rate of flow. If forests are cut off so that the rate of inflow is lessened, the river shrinks and flows in a smaller bed. The percentages of nitrogen, oxygen, and carbonic dioxide in the air are practically constant, because the income and outgo are practically equal. We have good evidence that there was once a time when the proportion of carbonic dioxide in the air was quite different from what it now is.

chloride, whose formula has been given above—SbOCl. We looked at this a moment ago as an oxychloride of antimony; and so it is; but there is another way of looking at it which is very suggestive, and has enabled us to understand some antimony compounds we should have hard work to understand otherwise. It can be viewed as *the chloride of the group SbO*, and there are some curious compounds containing antimony, oxygen and SO_4, which are regarded to-day as sulphates of the same group. One of them has the formula $(SbO)_2SO_4$. These are called *antimonylic* salts (the group SbO being called *antimonyl*), and the salt just cited is called *antimonylic sulphate.*

The most common of these salts is *tartar emetic*, which is used in medicine. It is a rather complex substance, but its nature will not be difficult to understand. In the first place, it is a salt of an acid we have not met with so far—tartaric acid, whose formula is

$$H_2(C_4H_4O_6).$$

Tartar emetic is believed to be derived from this acid by the replacement of one of the two replaceable hydrogen atoms by potassium and the other by antimonyl, thus:

$$K\,(SbO)(C_4H_4O_6).$$

All three of the oxides of antimony act as acid-formers, and dissolve readily in alkalies, forming salts.

Bismuth resembles antimony very strongly, in so far as antimony acts as a metal. It forms salts which are rather more stable and crystallize better than the corresponding antimony salts. They are, however, more or less broken down by water, with the formation of basic salts; that is, salts in which the acid ion is partially replaced by oxygen or by hydroxyl. The chloride breaks down thus:

$$BiCl_3 + H_2O = 2HCl + BiOCl.*$$

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* In this, as in the corresponding antimony compound, it will be seen that two atoms of chlorine have been replaced by an oxygen atom.

One of the basic nitrates of bismuth is much used in medicine. Its formula is $Bi(OH)_2NO_3$, and it is called *subnitrate of bismuth.*

The compound obtained as above by decomposing bismuth chloride with water is called bismuth oxychloride, or sometimes *bismuthyl chloride,* as if it were the chloride of the group BiO. There are salts of other acids which, as in the case of antimony, are regarded as salts of this same group.

Only one of the bismuth oxides shows any signs of being an acid-former, and that is the highest one, Bi_2O_5. This is a point frequently noticed, namely, that if any of the oxides of an element show acid-forming tendencies, it is among the highest oxides that the tendency appears.

LECTURE 41.

PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH, AND THEIR MOST IMPORTANT COMPOUNDS.

PHOSPHORUS is a decidedly interesting element. It was first prepared in 1669 by Brandt, and is at present manufactured, at the rate of about 2500 or 3000 tons a year, mostly in England and in France. It is obtained almost entirely from bones, which consist mainly of a phosphate of the metal *calcium* having the formula $Ca_3(PO_4)_2$. The reactions are rather too complicated to give here; but the final process consists in heating a purified phosphate of calcium in retorts with carbon in the form of ground coal or charcoal. The phosphorus comes over as vapor; and is collected in water. Before being sent into the market it is remelted under water (it melts at 44°), and while in that condition is run into cylindrical moulds in which it solidifies; so it is generally met with in the form of round, yellowish-white sticks, which break with a fracture much like that of barley-candy, and are cut quite easily by a sharp knife.

It is a deadly poison when taken internally, and the vapor, even in small quantities, is capable of producing very bad effects when inhaled. Workmen in phosphorus factories are subject to a peculiar disease of the bones caused by phosphorus poisoning.

When heated in the air phosphorus takes fire at 50°, and even if simply exposed to the air at ordinary temperatures the oxidation is sometimes energetic enough at its surface to cause it to ignite; accordingly it is always kept under water, and should never on any account be either handled or cut except under water. It is an exceedingly dangerous substance.

When phosphorus is exposed to sunlight under water the color of its surface darkens, passing through different shades of yellow and orange until it is maroon-red. Again, if common phosphorus (which is often called "yellow phosphorus") be heated to 300° in a sealed tube filled with nitrogen, it rapidly undergoes the same color change, only the change is not a surface change, but affects the whole mass. The comparison between this red substance and the original yellow phosphorus is given below:

YELLOW.	RED.
Very poisonous.	Not poisonous.
Melts at a low temperature (44°).	Does not melt easily.
Very easily ignited (50°).	Not easily ignited (261°).
Soluble in bisulphide of carbon.	Insoluble in bisulphide of carbon.
When burned in oxygen gives an oxide of formula P_2O_5.	When burned in oxygen gives an oxide of formula P_2O_5.

It will be noted that the only respect in which the two agree is the last one, and this is the key to the whole situation; for it shows that we are dealing in both cases with phosphorus and nothing else, and brings us for the first time face to face with the fact that the same element can exist in several forms, which may be very different in physical properties, and which may vary as to the intensity of their chemical action.

When phosphorus is heated to a high temperature with metallic lead in sealed tubes, it undergoes another set of changes, and on cooling the tube, is found coating the lead in the form of black, glittering crystals with decidedly metallic lustre. This proves to be simply another form of phosphorus. It is interesting to note how the phosphorus in this form begins to show faintly the outward appearance of a metal. In fact, this form is sometimes called *metallic phosphorus*. Here, then, we have three distinct individual forms of phosphorus. There are numerous other cases like this. Some of them have been studied quite carefully and successfully, and these studies will be referred to in the proper connection. In some cases there is reason to think that the difference is due to a difference in the structure of the molecules with reference to the number of atoms in the molecule and the manner in which the atoms are arranged in the molecule. We have, however, no definite knowledge as to the present case. The red form of phosphorus is very important; for it can be used for practically all the purposes for which yellow phosphorus is used, and with far greater safety.

Aside from its uses in the laboratory, phosphorus is used mainly in the manufacture of matches. The mixtures which are used for coating the tips of matches are composed of three kinds of material. One thing is always phosphorus; then there is always some substance rich in oxygen, and which gives up its oxygen on small provocation; and finally there is some inactive substance, or mixture of substances, which simply serves as a kind of cement or "filling." For instance, the oxidizing agent may be manganese dioxide, or one of the higher oxides of lead. Some of the neutral substances used are chalk, lampblack, and some form of glue. The so-called "safety-matches" are made in such a way as to have the oxidizing mixture and the phosphorus separated; one being on the match-head, the other on the paper on which the match has to be rubbed in order to light it. The phosphorus (which is always the red form) is usually put on sand-paper. The match-heads consist of a mixture of oxidizers such as potassic chlorate, the red oxide of lead, etc., with sulphide of antimony. This mixture will ignite only when drawn across the specially prepared paper.

COMPOUNDS OF PHOSPHORUS.

The hydrogen compounds of phosphorus are of no particular importance. The simplest one, PH_3, called *phosphine*, *phosphuretted hydrogen*, or *hydrogen phosphide*, is a colorless gas, which may be obtained by heating yellow phosphorus in a small retort with strong NaOH or KOH solution.* The gas which comes off takes fire on exposure to the air and burns with the formation of a dense white smoke of phosphoric oxide. It is known, however, that this spontaneous ignition is caused by the presence of another phosphide of hydrogen, which is formed in this reaction in small quantities. PH_3 does not dissolve very readily in water; and the weak solution of the gas in water is not alkaline, as in case of NH_3, the corresponding nitrogen compound, but there are some curious compounds which appear to be attempts on the part of the phosphorus to imitate the ammonium salts. The best known one has the formula PH_4I, and is called *phosphonium iodide*. It is analogous in formula to NH_4I. Only a few of these salts are known.

OXIDES OF PHOSPHORUS.

There is not much to be said of the two oxides of phosphorus. They are both white, snow-like bodies, which are formed when phosphorus burns in the air. If there is a limited supply of air, P_2O_3 is formed. If there is an abundant supply, P_2O_5 results. Both of them react vigorously with

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*A small *tubulated* retort is fitted at the tubulation with a smooth rubber stopper, through which passes a small tube connected with the gas supply. To the end of the retort neck is adapted, by means of another stopper, a small delivery-tube dipping under water. Fill the retort half full of strong NaOH and add about 3 grams of yellow phosphorus. Run coal-gas through the apparatus for several minutes, to sweep out the air. Then turn it very nearly off, and carefully heat the contents of the retort to boiling.

water. P_2O_5, which is called *phosphoric oxide*, *phosphorus pentoxide*, or *phosphoric anhydride*, is often used in drying gases. It acts in this way more decidedly than concentrated sulphuric acid.

THE ACIDS OF PHOSPHORUS.

Phosphorous acid results from the action of water upon P_2O_3:

$$P_2O_3 + 3H_2O = 2\ H_3\ PO_3.$$

It is not of enough importance to merit further mention

The phosphoric acids are of more interest. There are three of them, and their salts are many and important.

When we dissolve P_2O_5 in cold water we obtain a solution from which can be isolated a substance having the formula HPO_3, and this is an acid analogous in structure to HNO_3. This acid is called *metaphosphoric acid.* When it is boiled with water it undergoes change, and the solution on evaporation yields another acid having the formula H_3PO_4. This formula differs from that of metaphosphoric acid by one molecule of water, and consequently the boiling with water seems to have resulted simply in hitching on a molecule of water in some way. This second phosphoric acid is a very well-defined acid. It is called *orthophosphoric acid*, or *ordinary phosphoric acid*, and is the acid whose salts constitute the naturally occurring phosphates.

Phosphoric acid is a good representative of the acids containing oxygen. The most important knowledge we have gained of these acids is that some of the hydrogen and oxygen present is in the form of *hydroxyl groups*, and that it is the hydrogen of these hydroxyl groups which is the so-called "replaceable hydrogen" of the acid. The evidence is simply that experience shows that wherever an hydroxyl group is present in a molecule we can, by certain reactions, remove this group bodily and replace it by a single chlorine atom, and if we perform the reaction in question upon a substance, and find that an oxygen and a hydrogen atom have disappeared and that an atom of chorine has come in, we feel safe in deciding that an hydroxyl group is present. If we find that two oxygen and two hydrogen atoms have disappeared and that two chlorine atoms have entered, we conclude that two hydroxyl groups are present, and so on. The reagent used in this hydroxyl test is usually one of the chlorides of phosphorus, and the reaction is of great service in studying the constitution of the acids.

The case of phosphoric acid is a trifle peculiar. The line of argument which leads us to conclusions as to its structure will best be understood after a little study of the behavior of phosphorus pentachloride.

This substance, like the trichloride, is completely broken down by a large quantity of water, and in much the same way, but if the quantity of water added be relatively small the decomposition is only partial. Hydrochloric acid is given off, and an *oxychloride* results:

$$PCl_5 + HOH = 2HCl + POCl_3.$$

This oxychloride is a liquid which can be distilled off and purified without trouble; the interesting point about it is that when it is treated with more water all the chlorine goes out as HCl, and we find in solution *phosphoric acid*, whose formula differs from that of the oxychloride in that for every chlorine atom formerly present *a hydrogen and an oxygen atom have entered the molecule.* Thus,

$$POCl_3 + 3H_2O = PO(O_3H_3) + 3HCl.$$

The best interpretation we can give of this fact is that the oxygen and hydrogen have entered in form of hydroxyl groups, and that phosphoric acid contains three such groups. We may accordingly write the formula of phosphoric acid thus:

$PO(OH)_3$; and this formula serves to remind us of the results we have thus far reached.*

If we attempt to represent any more completely the manner in which this molecule is linked together, we find ourselves involved more or less in speculation; still we do constantly make such attempts; and whatever may be thought of them, they are decidedly a feature of modern chemical thought. So long as we continue to think of molecules as made up of atoms, we shall have to think of the atoms as held together in the molecule somehow. Moreover, when we are confronted with the fact that an atom of chlorine is united with a single atom of hydrogen in hydrochloric acid (HCl), that an atom of oxygen is united with two atoms of hydrogen in water (H_2O), that an atom of nitrogen is united with three atoms of hydrogen in ammonia (NH_3), and that in "marsh-gas" (CH_4) one atom of carbon is united with four atoms of hydrogen, we cannot help trying to find some way of representing to the eye this apparent difference of holding power among the elements. This matter was touched upon in a former lecture,† but we may as well look at the facts a little more in detail now. The chlorine atom is able to hold one hydrogen atom. The oxygen atom can hold or fix two. About this there is, according to our present light, no doubt. This fact can be represented to the eye thus:

$$Cl- \qquad -O-$$

and the formulæ of water and of hydrochoric acid may be written thus:

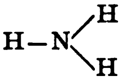
$$Cl-H \qquad H-O-H$$

---

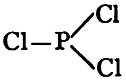
* It will be noticed that we have, in this case, made use of a reaction which is just the reverse of the one given above as a proof of the presence of hydroxyl groups. The results are just as valid, and the method is often convenient.

† See p. 236.

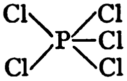
as if the chlorine and oxygen atoms were provided with hands or bonds of some kind, by which they could fix and hold other atoms. Ammonia can be written:



The chlorides of phosphorus thus:

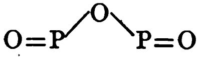


and

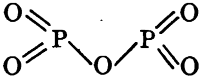


where the phosphorus atom manifests a different holding power (or *valence* as it is sometimes called) under different circumstances.

Further, remembering that oxygen has twice as much holding power as hydrogen or chlorine, we can write the formula of the oxides of phosphorus thus:



and

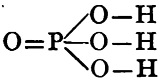


Let us see what will be the holding power, or valence, of the hydroxyl group. If a hydrogen atom and an oxygen atom unite thus,

$$-[O-H],$$

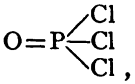
apparently one of the oxygen bonds is left free, and thus the hydroxyl group as a whole ought to show the same valence as hydrogen or chlorine, which it does—as the facts we have just been considering in case of phosphoric acid clearly show.

Can we now form any more definite idea as to the structure of phosphoric acid itself? Since it is obtained from phosphoric oxide (P_2O_5), in which the valence of phosphorus is clearly *five*, the probability is that the valence is the same in phosphoric acid. This, then, is our starting-point. We have found that there are three hydroxyl groups present, and these with an oxygen atom are grouped around the phosphorus atom in some way or other. The most simple and obvious grouping would be thus:



And this structural representation of phosphoric acid is in accord with all known facts.

The oxychloride, $POCl_3$, may be represented thus:



which brings out clearly the relation between the two substances.

One final point. It has previously been stated that when PCl_3 reacts with water it is completely broken down with formation of the corresponding hydroxide:

$$PCl_3 + 3H_2O = 3HCl + P(OH)_3.$$

When PCl_5 reacts with a large quantity of water we might expect a corresponding result; thus:

$$PCl_5 + 5H_2O = 5HCl + P(OH)_5.$$

As a matter of fact, however, we get, instead of this hydroxide, *phosphoric acid;* thus,

$$PCl_5 + 4H_2O = 5HCl + PO(OH)_3,$$

and the formula of phosphoric acid differs from that of the hydroxide, $P(OH)_5$, by one molecule of water. As we have seen, this is something frequently observed in dealing with hydroxyl compounds;* and all experience seems to indicate that compounds containing several hydroxyl groups attached to the same atom are very apt to split off parts of their hydroxyl as water.

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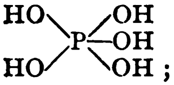
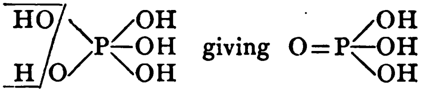
* Cf. p. 236, foot-note.

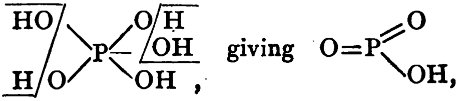
For example: When phosphorus is oxidized in contact with water (as by boiling with strong HNO_3), or when PCl_5 is treated with water, the product to be expected is $P(OH)_5$, or



but what seems to happen is that from this compound there splits off sometimes one molecule of water; thus



(ordinary phosphoric acid), or two molecules; thus



which corresponds to *metaphosphoric acid.* We shall often have occasion to notice this action.

LECTURE 42.

THE PHOSPHATES—ARSENIC, ANTIMONY, AND BISMUTH COMPOUNDS.

SINCE phosphoric acid has three replaceable hydrogen atoms, it is clear that with a metal like sodium, which has the power to replace only one hydrogen atom, we might expect to get three sodium phosphates, NaH_2PO_4, Na_2HPO_4, and Na_3PO_4. All these are known, and they can be prepared by the following reactions:

for monosodic phosphate,

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O;$$

for disodic phosphate,

$$H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O;$$

for trisodic phosphate,

$$H_3PO_4 + 3NaOH = Na_3PO_4 + 3H_2O;$$

that is, by mixing phosphoric acid and sodic hydroxide in the proportions indicated in the above reactions.

The same is found to be true in case of the phosphates of metals with a replacing power of two—like calcium; only most of these salts are derived from two molecules of phosphoric acid instead of one. The three phosphates of calcium are:

$CaH_4(PO_4)_2$, monocalcic phosphate;

$Ca_2H_2(PO_4)_2$, dicalcic phosphate;

$Ca_3(PO_4)_2$, tricalcic phosphate.

$Ca_3(PO_4)_2$ is called simply calcic phosphate, and is the most common of the phosphates occurring naturally. $CaH_4(PO_4)_2$ is sometimes called *calcic superphosphate*, and is the main constituent of artificial fertilizers. Both these compounds will be further noticed when we come to study the calcium compounds. We can pass from any one of the phosphates of sodium to the other by adding the requisite quantity of any acid, or of sodic hydroxide, as the case may require. For instance, to pass from disodic to trisodic phosphate,

$$HNa_2PO_4 + NaOH = H_2O + Na_3PO_4;$$

from trisodic to disodic phosphate,

$$Na_3PO_4 + HCl = NaCl + Na_2HPO_4.$$

The chlorides of phosphorus are made by treating phosphorus directly with chlorine. PCl_3 is first formed, and when this is treated with more chlorine PCl_5 results. PCl_3 is a liquid, PCl_5 is a whitish-yellow crystalline solid. They have to be kept in tightly-stoppered bottles, for the moisture in the air would soon decompose them. Their chemistry has already been sufficiently discussed.

ARSENIC.

The element itself is of no special importance. It is sometimes found free in nature, but is usually found united with some one of the metals, forming the so-called *arsenides*. Common "pyrite" often contains it.

Hydrogen Compounds.—The only one meriting mention is AsH_3, which is commonly called *arsine*. It is formed whenever an arsenic compound is brought into a solution in which hydrogen is being liberated, as the atomic hydrogen unites with the arsenic very readily. *The gas is deadly poison, and no person, except one who understands fully what he is about,* *and who is thoroughly experienced, should ever intentionally cause its production. No student should ever think of attempting it unless under the most detailed instruction and constant supervision of the teacher.*

When ignited, the gas burns with a livid-blue flame with the production of As_2O_3 and water; and when passed through a red-hot tube is decomposed into hydrogen which passes on, and arsenic which deposits upon the cooler portion of the tube as a lustrous coating sometimes brownish in color and sometimes steel-gray with high lustre.

The so-called "Marsh test" for the presence of arsenic consists in bringing a portion of the solution to be tested into a hydrogen generator, the exit-tube of which is provided with a platinum or pipe-clay jet at which the carefully-dried hydrogen is burning. When the solution is poured in, the flame becomes livid blue, and on bringing the bottom of a porcelain dish down over the flame (in the interior of which the AsH_3 is decomposed by the heat from the outer burning mantle) brownish spots of arsenic appear on the porcelain wherever the flame touches. This is, however, only a rough test. The Marsh-Berzelius method is much more sure and sensitive. This process is much like that just described, only the gas is led through a red-hot tube of hard glass which is drawn down to the thickness of a straw just beyond the flame. The arsenic deposits on the walls of this small tube, and the smallest trace is visible. Of course all reagents used either in getting the test substance into solution or in generating hydrogen must be absolutely free from arsenic; and no test is reliable until the operator has personally proved this to be the case by running the generator with the hot tube attached for an hour at least, and obtaining not the faintest trace of a "mirror" on the tube.*

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* Zinc, sulphuric acid, and nitric acid, free from arsenic, can now be obtained in the market if specified. The preliminary test should, however, always be run with every new lot of zinc or acid.

When food, paper, cloth, or the contents of a stomach are to be examined for arsenic, it is necessary to destroy the organic matter first. This is usually done by heating the material with concentrated nitric and sulphuric acids, by which means the organic matter is partially oxidized to carbonic dioxide and water, and partially charred; so that there remains, essentially, only the arsenic as As_2O_5 (easily soluble in water) and charcoal. The mass is then thoroughly extracted with water, and the solution brought into the generator.* Simple as it seems, this process is of value only in the hands of an experienced and skilful operator.

Arsenious oxide (*"arsenic"* or *white arsenic*) is a white substance formed by burning arsenic in the air, or on the larger scale, by "roasting" (or heating in contact with air) the naturally occurring metallic arsenides. The As_2O_3 goes off in form of vapor which condenses.

It is only slightly soluble in water, but dissolves in concentrated HCl.† It is more readily dissolved by boiling solutions of NaOH, KOH, Na_2CO_3, or K_2CO_3, with which it forms soluble *arsenites* of sodium or potassium. These *arsenites* are salts of *arsenious acid* (H_3AsO_3), whose formula is exactly analogous to phosphorous acid (H_3PO_3). If this be remembered it will make it much easier to keep the formulæ in mind. The reaction between arsenious oxide and sodic hydroxide gives sodic arsenite and water:

$$6NaOH + As_2O_3 = 2Na_3AsO_3 + 3H_2O.$$

Arsenious oxide is a violent poison; and all the arsenic compounds, without exception, are more or less so. A dose of about $\frac{2}{10}$ of a gram of arsenious oxide will usually prove fatal. The best *antidotes* for arsenic poisoning are magnesic oxide and freshly precipitated ferric hydroxide,* both of which form insoluble compounds with arsenious oxide.

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* See *American Chemical Journal*, Vol. 2 (1880), pp. 235–244.

† See p. 261 for the nature of this reaction.

When to solutions of an arsenite solutions of salts of other metals are added, the arsenite of the metal is precipitated. Some of these, particularly the arsenites of copper, are of commercial importance. Most of them are colored compounds, usually green or blue. Some are used as pigments. "Paris green," which has been extensively used as a potato-bug poison, is essentially an arsenite of copper.

Arsenic Oxide (As_2O_5) *and Arsenic Acid* (H_3AsO_4).—When arsenic is heated with a powerful oxidizing agent in water solution, reactions take place which are exactly analogous to those we have encountered in the oxidation of phosphorus under the same circumstances,† the final product being H_3AsO_4, or *arsenic acid.*

When this substance, which separates in colorless crystals on evaporating the solution, is heated to dull redness, it decomposes into arsenic oxide, As_2O_5, and water:

$$2H_3AsO_4 = 3H_2O + As_2O_5.$$

Arsenic acid readily gives up an atom of oxygen and passes into arsenious acid. It is therefore used as an oxidizing agent, particularly in the manufacture of the aniline dyes. It is also extensively used as a preservative by taxidermists and tanners.

Its extensive use in the manufacture of colors which are used in dyeing cloth and wall-paper is unfortunate, for recent researches demonstrate that the comparatively small quantity of arsenic contained in wall-papers and fabrics may prove an element of danger. When arsenic compounds exist in contact with certain ferments, the germs of which are present in the air of inhabited rooms, volatile compounds of arsenic result, and these seem to act very decidedly upon the mucous membrane of the body, giving rise to a great variety of disorders, varying with the constitution of the person attacked.

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* There are two hydroxides of iron, $Fe(OH)_2$ (ferrous hydroxide) and $Fe(OH)_3$ (ferric hydroxide). The latter is a red, gelatinous precipitate obtained by precipitating a solution of some ferric salt like ferric sulphate with ammonic hydroxide. It should be thoroughly washed with water.

† See p. 274.

In testing wall-papers or cloths for the often very small quantities present, the Marsh-Berzelius process is employed.

Arsenious chloride is a liquid obtained by treating arsenic with dry chlorine gas. Enough has already been said about it in another connection.

ANTIMONY.

This element is found in nature in the form of its sulphide, Sb_2S_3, which is called *stibnite*. The finest specimens are found in Japan; and consist of masses of long glittering, steel-gray crystals. The metal is obtained from it by roasting it in the air, thus forming the oxide, which is then heated with carbon (coal or charcoal).

The metal is white, brittle, and crystalline. It has no uses by itself, but enters into the constitution of a number of the artificially-prepared metallic mixtures or *alloys*. Two of the most common are type-metal (lead and antimony) from which type is made, and britannia metal (tin and antimony). It is also a constituent of some of the so-called *anti-friction metals* which are used in the bearings of steam-engines. It dissolves in a mixture of nitric and hydrochloric acid, forming (as is always the case when this mixture is used) a chloride of antimony; strong nitric acid simply oxidizes it. The oxides of antimony are not particularly interesting. Antimonious oxide (Sb_2O_3) can be made by heating antimony in the air or by oxidizing the metal with nitric acid and carefully drying the product.

Sb_2O_4 is obtained by following the same process, only igniting the product strongly in the air.

Antimonic oxide, Sb_2O_5, is best obtained by first making antimonic acid and then gently heating it.

The acids of antimony have the same relations to these oxides as in case of the oxides of phosphorus and arsenic; and the formulæ are perfectly analogous.

There are some curious compounds of arsenic and antimony in which the oxygen of the acids is replaced by sulphur. Thus we have

$$H_3AsO_3 \text{ and } H_3AsS_3,$$
$$H_3AsO_4 \text{ and } H_3AS_4.$$

Sodium salts of these acids are formed when the sulphides of arsenic and antimony are treated with sodic sulphide, just as sodium salts of the corresponding oxygen acids are formed when the oxides are dissolved in NaOH. The following reactions show the analogy:

$$\begin{aligned} As_2O_3 + 6NaOH &= 2Na_3AsO_3 + 3H_2O \\ As_2S_3 + 6NaHS &= 2Na_3AsS_3 + 3H_2S \\ As_2O_5 + 6NaOH &= 2Na_3AsO_4 + 3H_2O \\ As_2S_5 + 6NaSH &= 2Na_3AsS_4 + 3H_2S \end{aligned}$$

These salts are called *sulpharsenites* and *sulpharsenates*. They are soluble in water. The sulphides of other metals (with the exception of tin) are not affected by sodic sulphide, and these facts enable us to separate arsenic, antimony, and tin from other metals.

The chlorides of antimony are both colorless crystalline solids. *Antimonious chloride*, $SbCl_3$, is made by treatment of antimony with chlorine. *Antimonic chloride*, $SbCl_5$, is made by treating antimonious chloride with excess of chlorine in the cold.

BISMUTH.

This element is usually found free in nature, and only needs to be purified. It is principally used for making its compounds. One of its most common impurities is arsenic, and as some of the bismuth compounds are used in medicine, it is of course necessary that the arsenic be removed. For this purpose the metal is melted with potassic nitrate, which acts upon the arsenic as an oxidizer and converts it into potassic arsenate, which is dissolved and carried away when the melted mixture is treated with water. Bismuth is used mostly in alloys, particularly in making the so-called *fusible* alloys. The composition of some of these is given below, with their melting-points:

	Newton's Metal.	Rose's Metal.	Lichtenberg's Metal.	Wood's Metal
Bismuth..........	8	2	5	4
Lead.............	5	1	3	2
Tin...............	3	1	2	1
Cadmium.........	0	0	0	1
Melting-point......	94.5°	93.75°	91.6°	60.5°

As has already been stated, bismuth forms no hydrogen compounds.

The oxides deserve only brief mention.

Hypobismuthous oxide, BiO, is black.
Bismuthous oxide, Bi_2O_3, is yellow.
Bismuthic oxide, Bi_2O_5, is brick-red.

The only common one is Bi_2O_3, which can be made by dissolving the metal in nitric acid, evaporating and heating the residue. It acts in every way like a typical metallic oxide.

The salts of bismuth have no particular interest except a basic nitrate,* which is used in medicine as a remedy for dyspepsia. When mixed with olive-oil, it forms a good dressing for burns or scalds.

There is only one well-defined chloride of bismuth, $BiCl_3$, which is a white, crystalline solid prepared by heating bismuth in chlorine.

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* See p. 264.

LABORATORY WORK.

1. Convert 2 grams of disodic phosphate into trisodic phosphate.

2. Purify a little arsenious oxide by volatilizing it and condensing the vapor (or *subliming*, as it is called). Proceed as follows: Take two *clean, dry* watch-glasses. In one place about 0.2 gram arsenious oxide. Place the other one over it in an inverted position, and so that the rims are in contact all round. Heat now the lower watch-glass by a *low, steady flame several inches below the bottom of it.* After a while stop the heating; allow the whole to cool and carefully remove the top watch-glass. Examine the under side with a hand-lens, and make sketches of the crystals in your note-book.

3. Dissolve a little arsenious oxide (about 0.2 gram in about 3 c.c. of NaOH solution: just neutralize the solution with hydrochloric acid, and dilute with half its volume of water; then add a solution of cupric sulphate. Note the color, filter off the precipitate, wash it, and dry it in the air. It is cupric arsenite.

4. Treat a little powdered metallic antimony with concentrated nitric acid (5 or 6 c.c.) in a test-tube. *Very gently* warm the solution just enough to keep the action up, until the antimony has dissolved. Now boil the solution and note what happens. Can you explain what you have observed?

5. Wash a little of the white residue from the last experiment with water and dissolve it in about 6 c.c. of boiling concentrated HCl. Add some fragments of clean iron wire (card teeth) and boil for some time, keeping up the bulk of the solution by adding a little HCl from time to time. Finally, remove the fragments of wire, and filter. What is given off by the action of the acid upon the iron? See if you can find out what has been precipitated. (Try the action of acids upon portions of it. Heat a little on a porcelain cover. With the point of your penknife bore a small hole about ⅛ inch deep in a piece of charcoal. Pack it full of the substance, then close the holes at the base of your Bunsen burner and turn it down about two thirds. Turn the lamp so that the yellow flame covers the substance on the charcoal.) Sum up your facts. Can you come to any decision?

If so, can you give any explanation of the reaction by which the substance was produced?

6. Dissolve a little antimony in strong hydrochloric acid to which a few drops of strong nitric acid have been added. Pour the solution into cold water. What has taken place?

7. Prepare a solution of bismuthous nitrate by dissolving a little powdered bismuth in nitric acid with the aid of heat. Pour the solution into cold water. What is the product?

Also prepare a solution of the chloride. HCl will not dissolve bismuth appreciably, but on adding a few drops of HNO_3 the solution goes on rapidly, the *chloride* being formed. Pour the solution into water. What is the product? Write the reaction.

LECTURE 43.

OXYGEN AND SULPHUR.

We have now finished a systematic study of a metal group and of a non-metal group. We next proceed to consider another small group of non-metallic elements, partly because their compounds are very important and are met at almost every turn, and partly because it gives opportunity to bring to notice some more illustrations of matters we have just been studying.

The group in question consists of four members; but only two of them will receive any considerable attention. The other two are rarely met with, and their chief interest lies in their relationship to the two other members. Some of the group characteristics are tabulated below in the same way as in previous cases:

Element.	Symbol.	At. Wt.	State.	Melting-point.	Boiling-point.	Sp. Gr. (Solid).
Oxygen	O	16	Gas.	....	− 183°	......
Sulphur.	S	32	Yellow, brittle, solid	111°–114°	440°	2.045
Selenium	Se	78	Dark brown, solid.	217°	665°	4.5
Tellurium.. ...	Te	125 (?)	White, brittle, metallic, solid.	500°	......	6.25

We may notice first of all that in this group many of the same things appear as in the last; such as the increase in specific gravity and the change from gas to solid with rising melting-points and boiling-points as the atomic weight increases; and we shall see, as we go on, that starting with oxygen, a most decidedly non-metallic element, we end with tellurium, which begins to resemble the metals in outward appearance, though not at all in its chemical behavior.

There is a much more decided and striking relationship between sulphur, selenium, and tellurium than there is between any one of them and oxygen. One reason for this is easily seen. The principal compounds whose comparison has been most fruitful in results thus far have been the oxides, and naturally such compounds are wanting in case of oxygen itself.

LABORATORY WORK.

1. Examine and note carefully the color, odor, lustre, and texture of a specimen of sulphur.

2. Powder a very little in a clean porcelain mortar and try whether it is dissolved by either cold water or hot water. How will you ascertain whether any has dissolved? Put into a perfectly dry test-tube about 4 c.c. of carbonic disulphide,* add to it powdered sulphur as long as it dissolves freely. Filter the solution through a *perfectly dry* funnel and filter-paper into a 1½-inch dry crystallizing-dish, and allow the carbonic disulphide to evaporate off at the ordinary temperature and without being disturbed. Make careful sketches (of these crystals) † in your note-book.

3. Select a piece of sulphur weighing about 15 grams, of such dimensions that it will easily slip down into your graduated cylinder. Determine and record its exact weight; then proceed to determine its volume just as you formerly determined the volume of your cylinder, using, if necessary, your small graduated pipette, in order to get the volume accurately. Calculate now the weight in grams of one cubic centimeter (the density) of

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* Extinguish the Bunsen lamp while working with carbonic disulphide and see that there are no other lamps burning near by. The vapor of carbonic disulphide is very easily inflamed.

† In making such drawings the neatest method is to draw in the note-book, with the aid of a small watch-glass, a circle. Then pick out three or four good representative crystals and make within the circle *neat*, *clean-cut* drawings of them, *without any attempt at shading*, only attempting to copy *accurately* the telling lines of the crystal.

sulphur at the temperature of the water in which it was immersed.

4. Determine the melting-point of sulphur.

Take a small beaker (50 c.c. capacity) and two thirds fill it with a *clear*, saturated water-solution of calcic chloride. Mount it on the ring-stand with wire-netting and asbestos-paper. Next bend a short piece of thick copper wire into the form of a "stirrer," of this shape (see Fig. 47), the part *a* being a circle somewhat smaller than the inner diameter of the beaker. The part *b* serves as a handle. Place it in position in the beaker. By moving it gently up and down the liquid can be kept at nearly the same temperature throughout. Next take a piece of soft-glass tubing the size of a pencil. Heat it in the upper part of the Bunsen flame, turning it all the time until it softens decidedly and is red-hot; then draw the hands apart (not too rapidly) until the tube is about as thick as a match. Cut out a piece of this small tubing about 2 inches long; seal the end, and when cool fill it to a depth of about ½ cm. with powdered sulphur. Attach this small tube to your thermometer by means of a small band (cut from the end of a piece of rubber tubing) in such a position that the part holding the sulphur is close to the thermometer-bulb, the opening being, of course, uppermost.

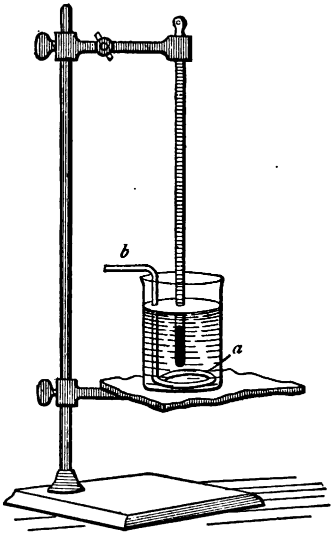

FIG. 47.

Clamp the thermometer in such position that the bulb dips into the liquid in the beaker with the bulb about ¼ inch from the bottom.

Since you have previously seen that sulphur does not melt in boiling water, it is clear that we can at once heat the contents of the beaker to 100° as rapidly as we please. Beyond that temperature, however, we shall have to heat much more cautiously.

Accordingly heat the beaker by means of a moderate flame, working the stirrer occasionally, until the temperature is within five degrees or so of 100°; then turn the flame very low and let the temperature rise at the rate of about one degree in ten seconds, working the stirrer constantly and keeping careful watch of the sulphur. The instant the sulphur begins to melt take away the lamp and at once note and record the temperature. If you do not make a thoroughly satisfactory determination the first time try again. Your first trial will, at least, have given you the melting-point within a degree or two. Make a sketch of your apparatus and record the result obtained. Save the stirrer for future use in similar determinations.

5. *Action of Sulphur upon Metals.*—Thoroughly mix five or six grams of "zinc-dust" with half its weight of finely-powdered sulphur. Make the mixture into a little conical pile on the asbestos-paper and heat the mass from underneath by a Bunsen flame. Note at once what happens. When the mass has cooled, place a little of it in a test-tube; add a few drops of dilute sulphuric acid and warm gently. Note the odor of the escaping gas; hold a piece of paper moistened with plumbic acetate in the mouth of the test-tube. Hold a match at or near the mouth of the test-tube. What happens? Again note the odor. Try now the same experiment with some of the original zinc-dust, also with the sulphur, carefully recording your results. Sum up now the *facts* established by this investigation. What do they suggest to your mind? If iron powder is available try the same line of experiments with it, mixing the iron and sulphur in the proportion of about 5 grams iron and 2.5 grams sulphur.*

Perhaps it will be just as well not to try to form a very definite idea of this reaction at present. We may get some side lights on it later. Let us take a look at the gas we have encountered in the course of these experiments. (That is, the gas we tried with lead-acetate paper.) Generate some of it in a 100-c.c. flask by treating some of the substance obtained by heating the mixture of iron and sulphur (it will be furnished you already made) with dilute hydrochloric acid. Connect the generator by means of a sleeve of rubber tubing and a small glass tube with a piece of hard-glass tubing about as thick as a pencil and 6 inches or so long, which has been *loosely filled* with asbestos-wool. To the other end of the hard-glass tube attach another small tube bent downward to the shape of a delivery-tube, and dipping under a solution of sodic hydroxide contained in a beaker or crystallizing-dish. The object of this latter is mainly to absorb the excess of gas which, as we have seen, has a disagreeable odor. Allow the gas to bubble through the alkaline solution until all air is swept out of the apparatus, which will be shown by the bubbles ceasing to come through, each one being completely absorbed. Then heat the hard-glass tube as hot as possible a little back of the middle, by one or two Bunsen flames.* What happens in the tube? What difference do you notice at the delivery-tube? Fill a ½-inch test-tube with sodic hydroxide and invert it over the delivery-tube. When it is nearly filled close it by the thumb, remove and shake; then turn it mouth upward and apply a match. Note odor, if any, and any other things that happen. What does the gas appear to be? What is the substance in the hard-glass tube? Just how much does this investigation tell you? Think it over very carefully. What have you obtained from this gas? Of what would it appear to be composed? See if the following adds anything:

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* The mixture may be heated in the bowl of a clay pipe, which makes an exceedingly handy crucible.

Take the same piece of hard-glass tubing; heat it in the middle in your lamp until it softens; then bend it a very little. When cool put into it a piece of sulphur the size of a large pea, and fill the front part of the tube with asbestos-wool. Mount the tube in position to heat (the middle of the tube should be lower than the ends). Connect it with a hydrogen generator. The delivery-tube simply vents into the air. Run hydrogen through until the air is thoroughly swept out; then carefully heat the sulphur with the Bunsen flame until it melts and turns very dark brown, almost black, and begins to vaporize slightly (the vapor is red-brown). From time to time note the odor at the delivery-tube, also the action upon "lead paper." Does this help you in deciding what this gas contains? Which is the most significant and satisfactory of the experiments you have made bearing upon this point?

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* The tube should be covered with a roof-shaped piece of asbestos-paper. It is also a good plan to wrap one thickness of copper-wire gauze round the heated part of the tube. The Bunsen lamps should be good ones, and if each student has only one, two can join forces on this piece of work.

Let us now see what we can do with the substances we obtained by heating metals with sulphur (see p. 288). We could not readily try many more experiments with the substances we have prepared by heating iron or zinc with sulphur, but there are some others which are rather easier to work with, and we will shift our ground a little and work with them. By heating antimony with sulphur a grayish mass is formed. You will be furnished some of this. Warm a little in a test-tube with strong hydrochloric acid, and note the characteristics of the gas that escapes. Then place five or six grams of the same substance in your hard-glass tube. Sweep out the air by hydrogen; then heat the tube red-hot with the Bunsen flame. Note the odor of the escaping gas and its action with lead-paper. What is left in the tube?

Sum up now all you have been able to find out about the products obtained by heating the metals with sulphur, and also about the gas evolved when one of these substances is treated with hydrochloric acid.

When sulphur burns in the air we have already seen that a gas with choking odor is formed; and that this gas dissolves in water with formation of a solution which is acid.* Since the burning was, in one experiment, performed in oxygen, it seems certain that we have in this solution an acid containing hydrogen, oxygen, and sulphur. *The same gas is given off when concentrated sulphuric acid is heated with metals such as copper.* In order to obtain some of this acid solution to examine, put a dozen inch-lengths of copper wire into a 100-c.c. flask provided with a cork and a delivery-tube dipping nearly to the bottom of a test-tube half filled with water. Add to the flask about 10 c.c. strong sulphuric acid, and heat gently until the gas bubbles through the water quite rapidly. When it has passed for about two minutes remove the test-tube, *still keeping up the heating*, and immediately replace it with another which is one third filled with a solution of sodic carbonate. Allow the gas to pass into this solution until it is no longer alkaline.

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* See page 118.

Test both these solutions for the SO_4 ion with hydrochloric acid and baric chloride in the usual way. Is SO_4 present? Warm about 1 c.c. strong nitric acid in a test-tube. Add to it a few drops of the solution you obtained by passing this gas into sodic carbonate solution. Heat to boiling; then cool, dilute with water, and test again with baric chloride as before. What is the result? In view of the powerful oxidizing action of nitric acid, what seems to be the relation between the acid now under study and sulphuric acid?

Let the solution you made in passing the gas into water stand *uncorked* until your next laboratory period, then test it again for SO_4.

Oxidation of Sulphur in Contact with Water.—1. Grind some "flowers of sulphur" with a little distilled water in a thoroughly clean mortar, for some minutes. Then throw the mass on a filter, and catch the water in a test-tube. Try its action upon blue litmus paper. Test for SO_4.

2. Boil a very little "flowers of sulphur" with about 2 c.c. strong nitric acid in a test-tube for two or three minutes. Dilute with water; filter, and test for SO_4.

LECTURE 44.

OXYGEN.

THE two great storehouses of oxygen are the atmosphere, where it occurs *mixed* with four times its volume of nitrogen, and water, where it occurs chemically combined with $\frac{1}{8}$ its weight of hydrogen. Oxygen is easily obtained from water by decomposing it by the electric current (first adding a little dilute sulphuric acid), but it is not so easy to get it from the air. Two methods have been proposed. One will be mentioned now, and the other will come up in another connection. The method to be described is based upon the following facts:

1. Oxygen is more soluble in water than is nitrogen. Water, then, when it dissolves air (as it does) dissolves relatively more oxygen than nitrogen, and the result is that the dissolved air is richer in oxygen than common air.

2. When air is compressed over water, the water dissolves more than it does at ordinary pressures.

3. When water containing dissolved gases is boiled, all the dissolved gas is, as a rule, expelled.

The method, then, is this: (1) Compress air over water and shake the two together, thus dissolving as much air as possible. (2) Boil the water, so as to expel the dissolved mixture of gases, which is now richer in oxygen than the original air. (3) Compress this mixture over water again, shaking as before. (4) Boil and expel dissolved gases again (this time still richer in oxygen). It is said that by repeating this process seven times a gas is obtained which is 97% pure oxygen. This process has never been commercially successful.

The most common method of preparing oxygen is by heating potassic chlorate. The gas thus prepared always contains traces of chlorine, and should be washed by passing it through water.

By whatever method it is prepared, pure gaseous oxygen is colorless and odorless. It is a little heavier than air. At 0° and 760 mm. 1 liter weighs closely 1.43 grams. When cooled to – 183° it condenses to a blue liquid.

The part played by oxygen in the economy of nature is very interesting and important. In the first place, it is essential to the existence of most forms of animal and some forms of plant life. The act of breathing consists of drawing air into the lungs, where the oxygen of the air passes through a series of rather complicated reactions, the ultimate result of which is that carbonic dioxide is formed, and this is what is expelled when the lungs contract. It is just as though part of the body, or at least the carbon, were burned directly in the air, forming carbonic dioxide. It is largely by this constant formation of carbonic dioxide in the body that the temperature of the body is maintained. There is a certain analogy between the human body and a steam-engine with its boiler. The constant consumption of carbon, with formation of carbonic dioxide, is exactly what takes place in the fire-box of a locomotive or on the grates of a stationary steam-boiler. There is, moreover, a very strong analogy between the engine in its relation to the furnace and the body in its relation to the lungs.

So far as can now be seen, the only part the nitrogen of the air plays is to dilute the oxygen, and thus moderate the rapidity of its action somewhat.

Again, oxygen enters directly or indirectly into almost all forms of decay. When an animal or a plant dies it is more or less rapidly acted upon by oxygen and water, the action being often intensified and sometimes set up by organized ferments. The ultimate result is the production of carbonic dioxide, water, nitric acid, ammonia, nitrogen, and other products.

When we wish to know how much oxygen a given *mixture* of gases contains, we generally proceed on the basis that a gas which is completely absorbed by yellow phosphorus is oxygen. Accordingly we allow a small stick of yellow phosphorus to stand for some time in a measured amount of the gas mixture, noting and measuring carefully the amount of shrinkage. We are generally safe in calling the shrinkage oxygen. No simple method can be given for determining the amount of oxygen in *compound* gases. If the question is simply whether a given gas is or is not oxygen, and if the properties of the gas are like those of oxygen, the only other gas for which it could be mistaken is *nitrous oxide*, in which wood, sulphur, phosphorus, etc., burn as readily as in oxygen, and with much the same appearance. There is one point, however, in which they differ, and that is in *their behavior toward nitric oxide.* If a little oxygen be brought into nitric oxide it instantly changes it to NO_2 or N_2O_4 (red). Nitrous oxide has no such effect upon it.

Ozone.—The air of a room in which an induction coil, or some other form of high-tension electrical machine, has been in operation for some time, has a peculiar odor. When acidified water is being "decomposed" by the galvanic current, the oxygen which comes off at the positive pole has the same peculiar odor. Further, whenever this odor is noticed, it is found that a piece of paper which has been moistened with starch-paste containing a little potassic iodide is invariably turned blue. These facts were first brought into prominence in 1840 by Schönbein.

Under some circumstances (during heavy thunder-storms) the same odor is said to have been noticed in the air, and strips of "iodized starch-paper" hung out exposed to the air show a faint blue coloration. When moist phosphorus oxidizes slowly (in a bottle containing not enough water to cover the phosphorus), the air within the bottle shows the same characteristics, and finally the same effects are produced when a hot glass-rod is brought into a beaker containing a few drops of ether.*

Schönbein called the gas possessing these properties ***ozone.*** He believed it to be a new oxide of hydrogen. Its true nature was not definitely established for thirty-two years. Sixteen years passed before Andrews (1856) proved that the gas could be transformed completely into oxygen by simple heating, and conversely, that pure, dry oxygen could be transformed into the new gas by the silent discharge from an induction coil. More definite results were very hard to get; mainly because the gas obtained by any of the known processes was very largely mixed with oxygen, and very hard to purify. There is no simple process by which a given quantity of oxygen can be completely transformed into ozone *in such a way that the ozone is available.* When a confined volume of oxygen is acted upon by the silent discharge oxygen is transformed into ozone, but the reverse action by which ozone is transformed back into oxygen sets in thus,

$$\text{Oxygen} \rightleftarrows \text{Ozone},$$

and as in so many other cases which we have studied, we soon reach a point where the two reactions just hold each other in equilibrium, and the relative proportions of oxygen and ozone undergo no further alteration. These conditions are reached when about one fifth of the oxygen has become converted into ozone. If, however, we introduce some substance capable of absorbing or dissolving ozone, equilibrium cannot be reached, and it becomes possible to convert all the oxygen into ozone; but in this case the ozone is not available. Decisive results were finally obtained only by indirect methods, which will not be described here in detail.† The chief facts established were these:

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* Most of these points can be easily illustrated on the lecture-table. See Newth's "Chemical Lecture Experiments," p. 29 *et seq.*

† See Roscoe and Schorlemmer, vol. I., p. 236 *et seq.* Also Newth, *Inorganic Chemistry*, pp. 176–178.

1. When a measured volume of oxygen is transformed into ozone there is a shrinkage in volume of one third,—that is three volumes of oxygen become two volumes of ozone. Conversely, two volumes of ozone become, on heating, three volumes of oxygen.

2. One liter of ozone weighs one and one-half times as much as one liter of oxygen.

3. When ozone acts as an oxidizer there remains a volume of ordinary oxygen equal to that of the ozone taken; that is, every molecule of ozone yields a molecule of oxygen. These facts all point in one direction, and seem to indicate very clearly that the difference between ozone and oxygen is simply in the number of oxygen atoms in the molecule,—the molecule of oxygen containing *two* and the molecule of ozone *three*. All the above facts are perfectly explained on this basis.

Since the molecule of ozone, on this supposition, is one and one half times as heavy as the oxygen molecule, it follows that one liter of ozone ought to be one and one half times as heavy as one liter of oxygen. Moreover, three volumes of oxygen ought to yield two volumes of ozone, thus

$$3O_2 = 2O_3;$$

that is, three molecules of oxygen become two molecules of ozone, or, in general, there will be two thirds as many ozone molecules as there were oxygen molecules; this means that the ozone will occupy two thirds the volume formerly occupied by the oxygen.

Finally, the behavior of ozone as an oxidizer is easy to understand. For example, it acts readily upon mercury, forming the oxide and liberating oxygen, thus

$$Hg + O_3 = HgO + O_2.$$

One atom of oxygen attacks the mercury; the other two forming ordinary oxygen. Clearly the volume of oxygen formed ought to be the same as that of the ozone taken.

Ozone then is *triatomic oxygen.* It is the best understood example of an element existing in two distinct forms. It may be that the difference between the three forms of phosphorus* is ultimately to be explained in some similar way, but we have no direct evidence bearing upon this point.

Although ozone usually acts as an oxidizer, there are one or two cases where it acts to *abstract oxygen.* The most marked case is its action upon argentic oxide, in which case *metallic silver* is formed, and a volume of ordinary oxygen equal to *twice that of the original ozone.*

The explanation is, however, quite simple. The atom of oxygen in argentic oxide is rather feebly held, and is seized by the atom of oxygen from the ozone molecule with the formation of a molecule of ordinary oxygen, metallic silver being set free; thus,

$$Ag_2O + O_3 = Ag_2 + O_2 + O_2.$$

One of the resulting oxygen molecules is formed, then, by the decomposition of the ozone molecules; the other by the union of the oxygen atom from the oxide with that from the ozone. Clearly, there ought to be twice as much oxygen by volume as there was ozone, and this is actually the case.

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* See page 266.

LECTURE 45.

SULPHUR.

SULPHUR has been known from the earliest times. It was ranked as one of the three "elements" by the alchemists and was believed to confer upon substances containing it the property of combustibility.

It occurs in nature abundantly, sometimes free, sometimes united with metals forming the metallic *sulphides*, and sometimes united with metals and oxygen in the form of the metallic *sulphates*, which are, as we have seen, the salts of sulphuric acid. Most of the free sulphur is found in volcanic regions, notably in Italy and Sicily, though some is found in Iceland, Japan, and Mexico. In all these regions it is found in the ground, sometimes in form of crystals, and sometimes pretty intimately mixed with the soil. The purest crystals available in large quantities contain about 3 per cent of earthy matter. The process by which the sulphur is extracted from the earthy mixture containing it is a rather crude one, and very simple in principle. It consists in piling the earth impregnated with sulphur in large heaps, partially covered with earth, and setting fire to the outer portions of the heap. The heat developed melts the sulphur in the interior, which runs down into trenches prepared to receive it. The crude sulphur is prepared for the market in various forms. It is usually heated in large earthen retorts until it boils. The vapor is then swept rapidly into a large, cooled chamber, where it at first condenses as a very fine dust or powder, which is called "flowers of sulphur." As the condensing chamber grows hotter the sulphur condenses to a liquid, which collects at the bottom of the chamber and is drawn off into wooden cylindrical moulds about 1½ inches in diameter. In this form it is called "roll-sulphur" or "brimstone."

Enormous quantities of sulphur are used in the manufacture of sulphuric acid. It is one of the constituents of gunpowder: many kinds of fireworks contain it. When caoutchouc (crude rubber) is mixed with sulphur, and carefully heated, the sulphur and rubber form a tough, elastic mass, called *vulcanized rubber*, which is the staple article from which almost all forms of rubber goods are manufactured; though other substances besides sulphur are sometimes used in the vulcanizing process.

The most curious thing about sulphur is that it shows in a high degree the tendency we have already noted in case of phosphorus and oxygen, namely, the tendency to appear in different modifications. There are four or five perfectly well-marked modifications known, and several others less common and important.

It is easy to prepare some of these forms, and it will be interesting to see what their points of difference are. Of course the differences are only physical, namely, differences in crystalline form, specific gravity, melting-point, and solubility. Chemically they are all essentially the same, as is shown by the fact that any reaction involving sulphur can be performed with one modification as well as with another.

Starting with the common roll-sulphur, we begin by placing some in a small beaker and carefully heating it to 120° by placing the beaker in an evaporating-dish containing oil, or calcic chloride solution, heated to that temperature. When all is thoroughly melted we remove the beaker and allow it to cool until a crust begins to form over the surface. This crust is then pierced and the beaker rapidly inverted so that the still liquid sulphur may run out into water. On examining the interior wall of the beaker we find it lined with fine needle-like crystals, which project in toward the center of the beaker. These crystals melt at 120°, while the ordinary form of sulphur melts at 114°. Their specific gravity is 1.96, while that of the ordinary form is 1.80. It is like the ordinary form in being easily soluble in carbonic disulphide. From the shape of its crystals it is called "prismatic sulphur."

If we melt some sulphur in a small beaker, or in the bowl of a clay-pipe, and if we raise the temperature of the melted sulphur, we notice that as the temperature rises the color becomes darker and darker until at about 250° it is almost black, and so thick and viscid that the beaker can be inverted without its running out. At a slightly higher temperature it becomes somewhat more fluid, and if we now pour it into water it forms a ropy, elastic, brown, translucent mass, which is called "plastic-sulphur." It is nearly insoluble in bisulphide of carbon and has a specific gravity of 1.95.

Finally, when solutions of the sulphides of sodium or potassium are allowed to stand in contact with sulphur, they dissolve some of it, and if acid be added to the solution thus formed, the sulphur is precipitated in an *amorphous* or non-crystalline form, and in such very fine powder that it remains suspended in the liquid, forming a whitish-yellow, milky mixture called "milk of sulphur," which is used in medicine. It is soluble in carbonic disulphide.

For convenience let us tabulate the properties of these different forms of sulphur:

Name.	Melting-point.	Sp. Gr.	Soluble in Carbonic Disulphide.
Ordinary.......	114°	1.80	Yes.
Prismatic......	120°	1.96	Yes.
Plastic.........	....	1.95	No.
Milk of Sulphur.	....	....	Yes.

When "prismatic" sulphur is allowed to stand for twenty-four hours or so, it becomes opaque, and on examination turns out to have changed back to the ordinary form. The opaque appearance is due to the fact that the crystalline form has undergone a change, and that the needle-like crystals, although they keep their outward shape, really consist of an immense number of little rhombic crystals of the ordinary form. This change takes place more rapidly if the crystals be scratched or rubbed. Plastic sulphur, too, changes back, after some time, into the ordinary form.

Oxides of Sulphur.—Only two of these will be mentioned. When sulphur burns in the air there is formed a gas with a choking odor. Since the same gas is formed when sulphur burns in pure oxygen it must be an oxide of sulphur.

The following data enable us to get at its constitution:

1. When a piece of sulphur is brought into a confined volume of oxygen and heated, it takes fire and burns, and the volume of the gaseous product is found, after cooling, to be the same as that of the oxygen; that is, there has been no shrinkage. This, of course, means that there are just as many molecules of the new gas present as there formerly were of oxygen, or, what is the same thing, that each molecule of the new gas contains a molecule (or two atoms) of oxygen.

The question now arises: with how many atoms of sulphur are these two atoms of oxygen united? The best answer is given by a molecular-weight determination. The gas is 2.24 times as heavy as air. In round numbers, one liter under standard conditions weighs 2.89 grams. Dividing this by 0.09 (the weight of one liter of hydrogen under the same conditions), we get 32, and this multiplied by two gives us for the molecular weight, 64. Since there are two atoms of oxygen present, we subtract 32 from the 64, and have remaining 32. Does this represent the weight of one atom of sulphur or of more than one? For our present purposes we can get a satisfactory answer by appealing to the law of specific heats. The specific heat of sulphur is closely 0.18, and if we divide 6.5 by 0.18 we obtain about 36. This is, of course, only an approximation to the true atomic weight of sulphur, but it is near enough to show us that the 32 left on subtracting the two atoms of oxygen as above represents one atom of sulphur and no more. The formula of the gas is, then, SO_2, and it is called *sulphurous oxide*, or, quite frequently, *sulphur dioxide*. It dissolves readily in water, forming an acid solution. The acid is a weak one, and has no power to dissolve metals, but it neutralizes alkalies and forms salts which are quite stable and definite, and whose analysis shows that they are derived from an acid having the formula H_2SO_3, which is accordingly called *sulphurous acid*, its salts being called *sulphites*. The sulphites remind us somewhat of the carbonates in their behavior toward acids. When a strong solution of a sulphite is treated with any one of the strong acids, there is a marked effervescence, and sulphurous oxide comes off. The explanation is that sulphurous acid can only exist in water solution up to a certain concentration, and when it is formed in solution in such quantity that the concentration is above the limit, the extra acid decomposes into gaseous sulphurous oxide and water, leaving a solution of sulphurous acid which is the strongest that can exist at that particular temperature. The hotter the solution the less will be the concentration of the remaining solution, and accordingly, if a sulphite be boiled with excess of hydrochloric or sulphuric acid, the sulphite is completely converted into the chloride or the sulphate thus:

$$Na_2SO_3 + 2HCl = 2NaCl + SO_2 + H_2O.$$

Hot nitric acid, or any other oxidizing agent, changes sulphurous acid into sulphuric acid as we have seen in the laboratory.

The main use of sulphurous acid itself is in bleaching silk, straw, and wool. The articles are moistened and hung in a room in which some sulphur is burned in an iron pan. This forms sulphurous oxide, which unites with the water with which the articles are moistened and forms sulphurous acid, which does the work. The bleaching consists in most cases in an abstraction of oxygen from the material to be bleached, the sulphurous acid being converted into sulphuric acid. Sometimes, however, the action is not so simply explained. Dry sulphurous oxide has no bleaching power, and this is satisfactorily explained when we find how difficult it is to make sulphurous oxide take up any more oxygen.

As to solubility, the sulphites are, as a rule, rather less soluble in water than are the sulphates. The most common sulphites are those of sodium and potassium, and they are made by passing sulphurous oxide into a water solution of sodic hydroxide or sodic carbonate. The sulphurous oxide and water together act upon the alkali as sulphurous acid.

$$\mathrm{Na_2CO_3} + \overset{(\mathrm{H_2SO_3})}{(\mathrm{SO_2} + \mathrm{H_2O})} = \mathrm{Na_2SO_3} + \mathrm{CO_2} + \mathrm{H_2O}.$$

Sulphuric Oxide and Sulphuric Acid.—Sulphurous oxide refuses to unite with more oxygen under any ordinary circumstances. When, however, a mixture of two volumes sulphurous oxide and one volume oxygen is passed through a tube containing *platinized asbestos-wool,** moderately heated, the two unite and form a volatile substance which condenses in the colder parts of the tube as a white, snow-like solid, whose analysis shows that it has the formula SO_3. The substance is called *sulphuric oxide*, *sulphur trioxide*, or sometimes *sulphuric anhydride*. It dissolves in water with a hissing sound, forming a strongly acid solution, which is *sulphuric*

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* Made by soaking asbestos-wool in platinic chloride solution and then heating to redness. The chloride is decomposed and the platinum remains, coating the asbestos threads.

acid. There is hardly anything more to say about sulphuric oxide; but sulphuric acid is an exceedingly important substance, and we shall be obliged to give it quite a thorough study. It is manufactured in enormous quantities, and is of fundamental importance in many manufacturing processes. Moreover, it is in some ways the most typical of the strong acids.

LECTURE 46.

MANUFACTURE OF SULPHURIC ACID—CONSTITUTION.

THE method by which sulphuric acid is made on the large scale is very different in principle from that employed in making the other acids. There we start with some convenient salt of the required acid and distil it with sulphuric acid; the result being that since the common acids are, as a rule, far more volatile than sulphuric acid, they distil over. There are plenty of naturally-occurring salts of sulphuric acid, but the difficulty is to find an acid with which to distil them. There is no cheap and available acid which has a higher boiling-point than sulphuric acid; so the method fails altogether, and we are forced to resort to a process which practically amounts to building up sulphuric acid from its elements.

We begin by burning sulphur in the air. This forms sulphurous oxide, and if we can change this to sulphuric oxide in presence of water we shall get sulphuric acid by the interaction of the sulphuric oxide and the water. But sulphurous oxide is not easily changed to sulphuric oxide. The only direct method has been mentioned above in connection with sulphuric oxide, and this method is not suitable for our present purposes; so it is accomplished with the aid of nitric acid vapor and certain of the oxides of nitrogen.

Large rooms are built and lined with sheet lead. Into these rooms, or *chambers* as they are called, are brought sulphurous oxide (usually made by burning sulphur in the air), steam, air, and nitrous fumes obtained by heating sodic nitrate with concentrated sulphuric acid. When the sulphurous oxide meets the steam it reacts with it, forming sulphurous acid, H_2SO_3, and then the nitrous fumes (which consist principally of nitric acid vapor and nitric peroxide) oxidize the sulphurous acid to sulphuric acid.

The reactions are complicated. The nitric acid reacts thus:

$$2HNO_3 + 2SO_2 + H_2O = 2H_2SO_4 + NO + NO_2.$$

The two oxides of nitrogen produced by this reaction, in contact with air and steam, convert more SO_2 into H_2SO_4. It is believed that the first step is the formation of the so-called *nitrosyl sulphuric acid*, $H(NO_2)SO_3$, crystals of which appear coating the walls of the chambers when the supply of steam is insufficient:

$$2SO_2 + NO_2 + NO + O_2 + H_2O = 2H(NO_2)SO_3.$$

This nitrosyl sulphuric acid is broken down by water thus:

$$2H(NO_2)SO_3 + H_2O = 2H_2SO_4 + NO + NO_2.$$

The important point is that there is liberated the same mixture of nitrogen oxides that we started with, and they can evidently react just as before with more SO_2 and so on; that is, the process is *continuous*, and for all we have seen up to this point a certain amount of nitric peroxide ought to be able to convert an indefinite amount of SO_2 into H_2SO_4. Practically, however, it is necessary to keep passing nitrous fumes into the chambers during the process. It will be remembered that air is brought into the chambers, but it is only the oxygen that is used. The nitrogen passes into a vent leading into a tall chimney. In going out it necessarily sweeps along more or less nitrous fumes with it. To be sure these can be and are recovered to a considerable extent; but there is a small outstanding loss which has to be made good. The process by which the nitrous fumes escaping from the chambers are recovered reminds us of the method employed for saving the HCl given off during the manufacture of sodic sulphate from sodic chloride in the Leblanc process. (See p. 200.) The escaping waste gases are made to pass up through a tower provided with shelves which are covered with coke. Over these shelves concentrated sulphuric acid is kept trickling, and this rapidly absorbs the nitrous fumes. By diluting the acid the nitrous fumes are again given up. This tower is called the *Gay-Lussac tower*, from its inventor.

The acid collects on the floor of the chambers. When it has reached a certain strength (about 64% of H_2SO_4) it is drawn off, for experience has shown that at this concentration the acid begins to absorb nitrous fumes so that it would not be economical to try to make it stronger by this process. This so-called chamber acid is strong enough for many purposes. A stronger acid is obtained by the use of the *Glover tower*, which stands at the end of the chambers opposite to the Gay-Lussac tower. It is of much the same construction as the latter, only the shelves are covered with broken tiling. At the top are two reservoirs; one contains "chamber acid," the other Gay-Lussac tower acid, saturated with oxides of nitrogen. These two acids are allowed to flow down over the tiling, where they are met by the hot sulphurous oxide fresh from the burners and on its way to the chambers. Three things happen:

1. The Gay-Lussac tower acid is diluted and gives up its nitrogen oxides which are swept on into the chambers by the sulphurous oxide, there to assist in the conversion of SO_2 into H_2SO_4.

2. The sulphurous oxide is cooled before passing into the chambers, since it gives up its heat to the acid.

3. The chamber acid is strengthened partly by the admixture of the stronger Gay-Lussac tower acid and partly by the evaporation of water from it by the hot sulphurous oxide.

The acid which flows out at the bottom of the tower is called "Glover tower acid." If a still stronger acid is wanted, the only way is to concentrate it by evaporation in large pans or retorts. These are made sometimes of lead, sometimes of glass, and sometimes of platinum. The lead pans do very well for concentrating the crude acid. A pure acid cannot be obtained because the acid, as it gets strong, attacks the lead somewhat. Glass is free from this objection, but it is dangerous, as the dishes frequently break. Platinum is far the most expensive as to its first cost, but it is very durable and is not attacked by the strongest acid. If a very pure acid is wanted the crude acid is carefully distilled. The strongest acid in the market contains about 2% of water.

Pure hydrogen sulphate is a colorless, oily liquid of sp. gr. 1.854. The crude acid has a faint brown or purple tint. When added to water[*] the mixture becomes very hot. Accordingly, when the strong acid is to be diluted, a convenient quantity of water should be measured out, and about one fifth its bulk of concentrated sulphuric acid poured slowly in, *in a thin stream, being stirred all the while.* The concentrated acid rapidly *chars* organic matter. Wood and paper, for example, blacken when exposed to its action, the reason being that part of the hydrogen and oxygen they contain is abstracted by the acid as water, while the carbon is left and shows itself by its black color. It acts also upon the skin and flesh, especially when hot, giving very painful burns. Finally, its vapor is injurious if inhaled, and accordingly the acid should never be evaporated or boiled unless under a good draft-hood.

Sulphuric acid is used in a great many manufacturing processes. We have seen how it is used in the manufacture of sodic carbonate, sodic sulphate, hydrochloric acid, and nitric acid. It is also extensively used in bleaching-works, in the manufacture of dyestuffs, and for many other purposes.

CONSTITUTION OF SULPHURIC ACID.[†]

That sulphuric acid contains hydrogen, sulphur, and oxygen is clearly shown by its decomposition products and by its mode of formation. It may be decomposed by running it a drop at a time into a tube of porcelain or platinum containing fragments of tiling or pipe-clay heated to bright redness; and when it decomposes, three products, and only three, always result, namely, *sulphurous oxide*, *water*, and *oxygen*. We have seen also that we can oxidize sulphur first to sulphurous oxide and then to sulphuric oxide, which in contact with water gives sulphuric acid. The only elements involved here are hydrogen, oxygen, and sulphur.

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[*] *Water should never, under any circumstances, be poured into strong sulphuric acid.*

[†] Note that for the purposes of this discussion we are merely considering sulphuric acid as a certain liquid having perfectly well-defined characteristics, and which we can always obtain by suitable methods.

Our next question is as to the proportions in which these three elements are present in sulphuric acid, and this question will be discussed quite thoroughly, because it is a case of average difficulty and will give a good opportunity for seeing how the chemist is obliged to use his resources. Keep clearly in mind that we have in our favor the fact that sulphuric acid is a substance which can be obtained pure whenever desired, and that it will always be possible to weigh out accurately any quantity of it we may require for our work.

Let us start now with the question how the percentage of hydrogen in sulphuric acid can be determined. The simplest method would seem to be to act upon a known weight of the acid *in water solution* with some metal which is capable of displacing and driving out the hydrogen. If we can find some metal which will act in this way sharply and completely—that is which will act so as to displace all the hydrogen of the acid present—we can then collect and measure the hydrogen and calculate its weight. The common metals such as zinc and iron do not act completely enough. The action drags along almost interminably, and the solution never becomes fully neutral. It will not do to try sodium or potassium, for although they would displace all the hydrogen as completely as could be desired, they also act upon water at ordinary temperatures as we have seen; and this fact ruins their usefulness in the present case. There is, however, one metal among the fairly common ones, namely magnesium, which as experiment shows will answer our purpose in a very satisfactory manner. It does not act upon water perceptibly at ordinary temperatures, but when brought into even a very dilute sulphuric acid solution, acts rapidly upon the acid with evolution of hydrogen, the solution finally becoming fully neutral. This point being settled, the next question is, how can we prepare a dilute sulphuric acid solution such that each cubic centimeter of it shall contain *a known weight of sulphuric acid?* The answer is easy. Experiment has shown that by taking a weighed quantity of pure hydrogen sulphate (H_2SO_4), dissolving it in water and determining the exact weight of sodic hydroxide needed to neutralize it, we arrive at the result that one gram of sodic hydroxide will just neutralize 1.225 grams of sulphuric acid. Practically, then, all we have to do is to take any dilute solution of sulphuric acid that may be available, and then, by means of a sodic hydroxide solution of known strength, determine what weight of sodic hydroxide is needed to neutralize a measured volume of the acid. Suppose, for instance, we have a solution of sodic hydroxide containing 0.1 gram sodic hydroxide in every cubic centimeter; suppose, further, that we find that 10 c.c. of the sulphuric acid solution requires, for neutralization, just 15 c.c. of the sodic hydroxide solution; then we have used $15 \times 0.1 = 1.5$ grams of sodic hydroxide, and we find the amount of sulphuric acid present by the proportion $1. : 1.225 :: 1.5 : x$.

In this case we find by calculation that $x =$ closely 1.84, and the amount of sulphuric acid in one cubic centimeter of this solution would be $\frac{1.84}{10} = 0.184$ gram. We can now measure out at will such a volume of this solution as will contain any desired weight of H_2SO_4.

There is still another method by which we can get at the quantity of actual sulphuric acid (hydrogen sulphate) in a water solution of it. It is sometimes a more convenient method than that just given. It depends upon the fact that when sulphuric acid is mixed with a solution of baric chloride, a heavy, white precipitate falls (baric sulphate), and that if sufficient baric chloride be used, every trace of sulphuric acid is used up in the formation of this white precipitate. We take a carefully weighed quantity of pure hydrogen sulphate, dissolve it in water and add baric chloride until the formation of a white precipitate ceases. We then collect the precipitate on a filter-paper, and wash it several times with hot water. Finally we dry it, heat it to redness in a crucible, and when cool weigh it.

We find in this way that one gram of H_2SO_4 yields 2.382 grams of baric sulphate. It will be clear now, from this fact, that all that is necessary in any case is to take a carefully measured quantity of any sulphuric acid solution and add a sufficient quantity of baric chloride, collecting and weighing the precipitate. From this weight we can easily calculate the amount of acid present. Notice carefully that *both these methods are entirely independent of all theories. They both depend upon properties of sulphuric acid which are perfectly definite and invariable.*

We now measure out a quantity of dilute sulphuric acid containing, say, 0.5 gram of real sulphuric acid. We place this in a suitable small flask provided with a delivery-tube, and add to it a quantity of metallic magnesium, collecting and measuring the hydrogen. We have now all the data for calculating the weight of hydrogen obtained and the percentage of hydrogen in H_2SO_4.

Next, how about the sulphur? There is no practicable method of taking out the sulphur from a known weight of H_2SO_4 and determining its weight, but we can do easily what amounts to the same thing,—*we can take a weighed quantity of sulphur, convert it into sulphuric acid, and see what weight of acid we obtain.*

Sulphur may be converted into sulphuric acid by heating it with concentrated nitric acid solution. All strong oxidizing agents which act in water solution convert sulphur into sulphuric acid more or less quickly. Nitric acid is probably the best, all things considered. If we weigh out 0.1 gram or so of finely-powdered sulphur and heat it gently for some time with strong nitric acid, the sulphur all disappears, and numerous experiments have shown (1) that the solution contains no sulphur compound but sulphuric acid, and (2) that none of the sulphur is evolved in the form of gaseous sulphur compounds. The action is somewhat more rapid if crystals of potassic chlorate be added from time to time. Our only remaining task is to determine how much sulphuric acid is present in the solution thus obtained. The first of the two methods given above is useless, for the solution contains nitric acid as well as sulphuric acid, and this is neutralized by sodic hydroxide in the same way as sulphuric acid is. The second method, however, works very well indeed, since nitric acid gives no precipitate with baric chloride. We proceed, then, to find, by this method, how much sulphuric acid the solution contains, when we can at once calculate the percentage of sulphur in sulphuric acid. We have now found the percentages of hydrogen and of sulphur.

There remains the oxygen, and there is no practicable method of determining the quantity of this directly. We are sure, however, that only hydrogen, oxygen, and sulphur are present, and therefore if we add up the percentages of sulphur and hydrogen and subtract the sum from 100 per cent we shall get the percentage of oxygen. In fact, this is a method which is frequently used for getting at the percentage of oxygen in its compounds, especially when besides oxygen there is more than one element present.

LABORATORY WORK.

Determine the percentage composition of sulphuric acid as just described.

Fit up a short, ¾-inch test-tube with a doubly-bored rubber stopper (or a sound, well-fitting cork). To one hole fit a delivery-tube, and through the other pass a piece of thin glass rod (or tubing with the end sealed) about 4 inches long and of such size that while making a tight joint it may be slipped up and down in the hole when the stopper is in place. Place in the flask enough dilute sulphuric acid (of known strength) to represent about 0.5 of a gram of the real acid. By means of a small rubber band attach to the lower end of the glass rod about five inches of magnesium ribbon, rolled up into a short, compact bundle. Draw up the glass rod until the magnesium is just under the cork. Add enough water to the acid in the flask to fill the flask about one quarter full. Place the stopper in position, and arrange the whole so that the delivery-tube dips under the mouth of a 250-c.c. bottle or flask over a pneumatic trough. Push down the glass rod until the magnesium is in the acid. Allow the action to go on until no more hydrogen is evolved. This point will be reached in about three quarters of an hour, but it will be just as well to let the whole thing stand until the next laboratory hour. Then remove the flask and measure the volume of hydrogen collected. Take the necessary thermometer and barometer readings, calculate the volume down to standard conditions, and afterward calculate its weight (1 c.c. of hydrogen at 0° and 760 mm. weight, .00009 gr.). From this calculate the percentage of hydrogen in sulphuric acid.

While the evolution of hydrogen is still in progress begin on the determination of sulphur.

Weigh out in a 2½-inch evaporating-dish, as carefully as possible, about 0.2 of a gram of "flowers of sulphur." Put into the evaporating-dish about 10 c.c. of the strongest nitric acid. Cover the contents of the evaporating-dish with a 2-inch funnel, which will prevent spattering. Apply heat, using a rather low flame. Add occasionally small crystals of potassic chlorate. The sulphur will gradually disappear. *This operation must be performed under the hood.*

When this has taken place, remove the funnel, rinsing it with water from the jet of your wash-bottle, allowing the rinsings to fall into the evaporating-dish. Then rinse the contents of the evaporating-dish into a clean 3-inch beaker, and add enough strong hydrochloric acid to bring the bulk up to about 30 c.c. Cover the beaker with a watch-glass and heat the whole till it is just on the point of boiling; then draw aside the watch-glass a little and add a strong, clear solution of baric chloride. Stir the contents of the beaker for a few minutes, then add more baric chloride and see if any more precipitate falls. When this test shows that all the sulphuric acid has been used up, heat the solution for ten or fifteen minutes nearly to boiling, stirring frequently. At the end of this time the precipitate ought to settle quite rapidly on removing the lamp and allowing the solution to stand quiet.

The next thing is to filter off, wash, dry, and weigh the precipitate.

Fold a good filter-paper so as to fit your funnel accurately. Wet it with distilled water and place it in position to filter into a clean beaker.

Pour the liquid standing over the precipitate into the filter first (it is not necessary that the precipitate shall have completely settled). Afterward rinse the precipitate onto the filter completely by means of the jet from your wash-bottle. Allow the filter to drain itself dry, then wash the precipitate by directing the jet from your wash-bottle at the top of the filter-paper and running spirally down the filter-paper until the filter is about one quarter full of water. Repeat this process about four times. (In very exact work it would be necessary to test and see whether the washing were complete. How would it be done?)

When the precipitate has drained dry for the last time set the funnel over a register or a steam-radiator to dry (if a drying-oven is not available). When it is *thoroughly dry*, weigh your porcelain crucible. Open out the filter-paper carefully, and scrape the precipitate as completely as possible into the crucible. Roll up the filter-paper into a compact wad. Place it on the inverted cover of your crucible and set fire to it. When it ceases burning, heat the cover from underneath till the paper is reduced to ashes; put the ashes into the crucible. Support the crucible on a pipe-clay triangle and heat it with its contents as hot as possible for fifteen minutes or so; then cool and weigh. From the weight of the precipitate calculate how much sulphuric acid there must have been in your solution, remembering that 1 gram sulphuric acid yields 2.382 grams of the precipitate. From the quantity of sulphur used and the quantity of sulphuric acid obtained calculate the percentage of sulphur in sulphuric acid. Finally calculate the percentage of oxygen by difference as above explained.

LECTURE 47.

CALCULATION OF FORMULA—CONSTITUTION OF SULPHURIC ACID, CONTINUED.

WHEN we have ascertained what elements are present in a compound and the percentages in which they are present, the next thing is to calculate the formula; and we will see how this can be done.

Suppose, for example, we have analyzed a compound and found its composition to be:

Sodium,	57.50 %
Hydrogen,	2.50 "
Oxygen,	40.00 "
	100.00 "

That is, that in 100 grams of the substance the ratio is

Sodium : hydrogen : oxygen :: 57.50 : 2.50 : 40.00.

This is the same thing as saying that if we could by any means isolate a single molecule of the substance and analyze it we should find the above percentages of sodium, hydrogen, and oxygen.*

This molecule evidently contains sodium, hydrogen, and oxygen atoms, and therefore the above percentages must stand to each other in the ratio

$$57.50 : 2.50 : 40.00 :: x \text{ atoms Na} : y \text{ atoms H} : z \text{ atoms O},$$

where x, y, and z represent numbers at present unknown.

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* Of course this assumes that we have good evidence that the substance we are dealing with is a simple compound and homogeneous, not a mixture of several compounds.

If now we divide each of these percentages by the atomic weight of the corresponding element, the three quotients will stand to each other *in the ratio of* the number of atoms of each element present. Thus we have

$$\text{Na}\ \frac{57.50}{23} = 2.50.$$

$$\text{H}\ \frac{2.50}{1} = 2.50.$$

$$\text{O}\ \frac{40.00}{16} = 2.50.$$

These three quotients are equal, and this shows us that there are the same number of atoms of sodium, hydrogen, and oxygen. Therefore, the simplest formula possible would be $NaOH$. This is, however, as far as we can reason, for we have thus far no means of knowing whether the formula is $NaOH$, $Na_2O_2H_2$, or $Na_3O_3H_3$, or perhaps even more complex. A molecular-weight determination of some kind would be necessary to settle this point.

At all events, it will be seen that having the percentage composition of sulphuric acid we can calculate its *simplest* formula. Its molecular weight is not easily determined, owing to the fact that its vapor *dissociates* when it is vaporized, —that is, it decomposes into equal volumes of water vapor and sulphuric-oxide vapor. One molecule thus produces two new ones, and if the dissociation is complete there are twice as many molecules present as there were before, and these, of course, distribute themselves through twice the volume. In other words, if we should weigh out x grams pure sulphuric acid and vaporize it in a flask of such size that it would just be filled by the vapor of the acid, then *if no dissociation took place*, and if the volume of the flask were y c.c., the density of the vapor would be $\frac{x}{y}$. If, however, the vapor were wholly dissociated there would be twice as great a volume of vapor formed, and when the acid was finally all vaporized and we sealed up the flask we should have only sealed up half the acid we vaporized, so that our density would come out $\frac{\frac{1}{2}x}{y}$, or one half what we got before.*

When, however, in a case like this, the difficulty is fully recognized and carefully studied, it is possible to arrive at results wherein the error is eliminated, and in case of sulphuric acid the results point to the simplest possible formula.†

We now come to the final question and the most difficult one of all, namely, how are the atoms of hydrogen, oxygen, and sulphur linked together in the molecule H_2SO_4? On such a question we have no really direct evidence, but there is considerable circumstantial evidence which leads us to a view which seems highly probable and reasonable.

The most important pieces of evidence are these:

1. When sulphurous oxide (SO_2) is treated with gaseous chlorine the two unite and form a *liquid*, which upon analysis proves to have the formula SO_2Cl_2. It is called *sulphuryl chloride. When this substance is treated with water, hydrochloric acid is given off, and on concentration a liquid is obtained, having the formula* SO_4H_2 (or H_2SO_4) *and identical in every respect with sulphuric acid.*

What this means is, that for every chlorine atom that has gone out of the sulphuryl chloride molecule an oxygen and a hydrogen atom have come in, and, as has been previously stated, all our experience leads to the conclusion that this is a reaction which always marks the entrance of hydroxyl groups, ‡ and hence it seems very probable that sulphuric acid contains two hydroxyl groups. Further evidence is afforded by the decomposition of sulphuric acid. When dropped upon red-hot tiling, porcelain, or pumice-stone it decomposes with formation of steam, sulphurous oxide, and oxygen, in proportions corresponding with those indicated by the reaction

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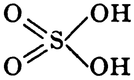
* See p. 169 for a parallel case in determining the molecular weights of substances in solution.

† Calculate from the average of the class results the formula of sulphuric acid.

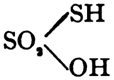
‡ See p. 270, where the same reaction was made use of.

$$H_2SO_4 = H_2O + SO_2 + O.$$

Since sulphuric acid always decomposes in this way, it seems probable that the molecule is so made up that two oxygen atoms are bound to sulphur directly, and stay so bound even in the above decomposition. The appearance of water and oxygen is what we might expect if two hydroxyl groups are present. From these and other considerations the conclusion has been drawn that in sulphuric acid the "valence" of sulphur is 6, and that the molecule is made up thus:



Another sulphur acid, which will be mentioned on account of one of its salts, which is of some importance, is *thiosulphuric acid.* Its salts are called *thiosulphates.* Its formula is believed to be



$$SO_2\begin{cases}SH\\OH\end{cases}, \text{ or } H_2S_2O_3.$$

It is sulphuric acid, in which one of the hydroxyl oxygens has been replaced by sulphur. Its sodium salt is called *sodic thiosulphate.* Its commercial name is *hyposulphite of soda*, and it is extensively used by photographers under the name of "hypo." It is used to "fix" the negative after the "developer" has been applied and the plate washed. The "fixing" consists in dissolving off from the plate the unchanged silver chloride or bromide. The dissolving takes place because the thiosulphate reacts with silver chloride to form a salt, $NaAgS_2O_3$, which is soluble. The thiosulphates can be easily recognized from the fact that, when treated with hydrochloric acid, sulphur is precipitated as a whitish-yellow powder, while at the same time sulphurous oxide is given off and can be recognized by the smell.

Hydrogen Sulphide, or *Hydrosulphuric Acid.*—Whenever animal substances containing sulphur (of which albumen is the most common representative) decay out of contact with air, there is obtained, among other things, a light, inflammable, disagreeable-smelling gas. When, for instance, an egg (which contains considerable albumen) decays, this gas results, and the odor of a rotten egg is largely due to its presence. Again, in the mud at the bottom of shallow, stagnant pools, ponds, or other bodies of water, the same gas is formed by the decay of shell-fish and other small animals, and when the mud is stirred up the bubbles which rise to the surface will generally have a strong odor of this same gas. Finally, it is formed under the surface of the earth by reactions which we can understand better after a little study of the gas. Under these latter circumstances it is dissolved by water and carried on until it finally emerges somewhere as a *sulphur spring*, the so-called "sulphur waters" being simply solutions of this gas in water.

It can be made in the laboratory by the action of acids upon metallic sulphides, and we have already come across it in course of our laboratory work. Its odor, as thus obtained, is not so disagreeable as when it results from decay. The most convenient way of securing large quantities of it is to treat a sulphide of iron having the formula FeS with dilute hydrochloric or sulphuric acid.

CONSTITUTION.

The fact that this gas can be made by passing hydrogen over heated sulphur sufficiently shows what it contains.*

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* See Laboratory Work on Sulphur Compounds, p. 289.

The question as to its quantitative composition is settled by (1) the fact that when a measured volume of it is passed over heated tin it is decomposed with liberation of a volume of pure hydrogen equal to the volume of the original gas, and (2) that one liter of it, under standard conditions, weighs closely 1.33 grams, or about seventeen times as much as the same volume of hydrogen. This points to a molecular weight 34; and, since the experiment above quoted shows that one molecule of the gas contains two hydrogen atoms (how does it show this?), it follows that the formula is H_2S.

The gas dissolves in water; one volume of water dissolving about three volumes of the gas at ordinary temperatures. The solution *reacts acid*, and is called *hydrosulphuric acid.* When added to solutions of most metallic salts it precipitates *sulphides*, or salts of hydrosulphuric acid. The same results are obtained when the gas is caused to bubble through the solution of the metallic salt. Most of these metallic sulphides are, as we have seen, insoluble.

The gas is, as above stated, formed under the surface of the earth. It is probably formed by two reactions, (1) the transformation of metallic sulphates to sulphides by organic matter, and (2) the action of weak organic acids upon the sulphides thus formed.

By whatever means formed, the gas is, even when considerably diluted, poisonous, and should never be generated in any considerable quantity unless under a good hood. In dilute water solution, as in the sulphur waters, it has a very decided medicinal value. When the solution is allowed to stand, it is acted upon by oxygen in such a way that sulphur separates and water is formed, probably thus

$$H_2S + O = H_2O + S.$$

We have already seen that the gas burns in the air, and that one of the products is sulphurous oxide; the other product is, of course, water:

$$2H_2S + 3O_2 = 2H_2O + 2SO_2.$$

LABORATORY WORK.

Prepare and wash a little argentic chloride. Place a little in a test-tube, add one or two c.c. of a strong solution of sodic thiosulphate and shake.

To a solution of sodic peroxide in water add just enough dilute hydrochloric acid to make it faintly acid. This solution has great oxidizing power. Divide it into two parts. Pass a current of hydrogen sulphide through one part for some minutes. Then add the other half and make a test for the presence of the SO_4 ion.

What has taken place?

Place in a test-tube a few c.c. of a strong solution of bromine in water. This also is a powerful oxidizer. Pass H_2S through the solution until the color of bromine disappears. Test for the SO_4 ion. What has taken place? Never mind how either of these oxidizers work. Simply consider that by their agency oxygen is caused to act upon the hydrogen sulphide.

Reduction of Sulphurous Acid to Hydrogen Sulphide.—When sulphuric acid is heated with sulphur, carbon, or some metal like copper, a rather complicated set of reactions takes place, the most prominent product being SO_2. When this is passed into water, it gives, as we have seen, H_2SO_3, whose formula differs from that of sulphuric acid in having one oxygen atom less. Can we remove the rest of the oxygen and get H_2S? Let us see. One of the best agents for removing oxygen from substances in solution is *hydrogen generated right in the solution.* Under these circumstances the hydrogen comes in contact with the substance just at the instant of liberation, and before the hydrogen atoms have united to form hydrogen molecules.

Place in a test-tube a little zinc and dilute hydrochloric acid, and when the evolution of hydrogen is well under way add a piece of sodic sulphite the size of a small pea. Heat nearly to boiling and note the odor. The best way to detect small quantities of hydrogen sulphide is by holding in the mouth of the test-tube or generator from which it is coming, a strip of filter-paper, moistened with a solution of plumbic acetate. Such paper is by hydrogen sulphide turned brown or black, according to the quantity present.*

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* When the balloon used by Andrée in his recent (apparently fatal) expedition was being fitted up it was necessary to find and stop all leaks. The balloon was filled with hydrogen. Now hydrogen, prepared by the action of dilute sulphuric acid upon zinc, contains small quantities of hydrogen sulphide. Therefore, in searching for leaks, strips of paper moistened with plumbic acetate were spread over the seams, and wherever the paper darkened a leak was located.

LECTURE 48.

CALCIUM, STRONTIUM, AND BARIUM.

WE now return to the metallic elements again; and our plan is the same as has been followed in our previous studies, namely, to study a metal which is a good representative of a new group or family; and the metal we will first consider is calcium. The metal itself is only a laboratory curiosity and is very rarely seen; indeed, it has probably never been prepared in the pure state until recently.* It is silver-white with a fine lustre. The method by which it is best prepared is perhaps worth considering briefly as an application of principles. When calcic iodide is heated to redness in a carefully closed iron crucible with excess of metallic sodium, there are formed sodic iodide and metallic calcium which dissolves in the excess of sodium. When, however, the crucible is cooled the calcium crystallizes out from the molten sodium, for although sodium dissolves calcium quite freely at a red heat, it dissolves hardly any at lower temperatures. It is just like crystallizing a salt from water.

The cake of metallic sodium is now treated with pure alcohol, which dissolves the sodium, but leaves the calcium behind as a brilliant white crystalline powder.

The metal is about one and one-half times as heavy as water, tarnishes rapidly on exposure to moist air, and decomposes water violently with evolution of hydrogen.

The compounds of calcium are very abundant and important. The carbonate occurs in no less than five well-defined forms, among which the most important are *limestone*, *chalk*, and *marble.* These will be considered in more detail later. The most common natural form of the sulphate is *gypsum.* The phosphate is called *apatite* and is used in making fertilizers. Calcic phosphate is also the main constituent of bones.

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* See *Chemical News* for July 22, 1898, p. 37.

In studying these compounds the best starting point is the carbonate.

The most common form of it is *limestone,* which is a light-colored, compact rock found in large quantities in many parts of this country and Europe. It is one of the most valuable and durable of building-stones. That it is not easily dissolved by water goes without saying. It is probable that all our enormous deposits of limestone have been brought by water to their present places and deposited, during enormously long periods of time, in the form of so-called *sediments,* or precipitates on a very large scale. These sediments are believed to have become cemented together into solid rock under the influence of heat, pressure, and water. These three agencies have acted to different extents in different places. In some localities the effects have been very pronounced and the limestone has been converted into a semi-crystalline *marble,* the color of which varies. If the limestone was pure, we have white marble ; if impure, colored or variegated marble results.

In the crevices and fissures of limestone quarries there are occasionally found beautiful rhombic crystals of calcic carbonate. These crystals are quite transparent when pure, and, when struck with a hammer, break into fragments which are the same shape as the original crystals. This form of calcic carbonate is called *Iceland spar,* and it is chiefly interesting from the fact that it gives double images of objects viewed through it, and is hence said to have the power of *doubly refracting* light.

Chalk consists mostly of the shells of microscopic shell-fish. These accumulate to immense depths at the bottom of the ocean, and most of the chalk deposits we now use have come into being by some movement of the earth's crust resulting in a portion of the sea bottom rising above the sea-level, and thus becoming land.

Coral is a very beautiful form of calcic carbonate deposited on the bottom of the ocean at moderate depths by the coral polype. The deposit left by each individual serves as a foundation for others to build on, and thus there sometimes accumulate enormous reefs and islands of coral. It is of varying colors, and its most characteristic form is a tree-like growth. The whitest form is almost pure calcic carbonate.

Shells consist mainly of calcic carbonate.

In limestone deposits there often occur caves of more or less extent. Water generally drips from their roofs, and this water is apt to be charged with calcic carbonate. As it comes out into the air it slowly loses its charge of calcic carbonate for reasons which will soon appear. The result is, that where the water drips a sort of icicle formation begins. These calcic-carbonate "icicles" are called *stalactites*, and are exactly like icicles in shape.

The uses of marble and chalk are well known and need not be mentioned here. Limestone is rather more interesting from our present point of view, for in order to make it ready for some of its most important uses it has to undergo some chemical transformations. These transformations and other matters connected with the calcium compounds will be better understood after a little work with them in the laboratory.

LABORATORY WORK.

The most important calcium compounds are the carbonate, oxide, hydroxide, chloride, and phosphate. We will take them in the order named:

1. Weigh carefully a piece of white marble. (The piece

should weigh *about* one gram.) Hang it by a piece of platinum wire so that it stands just above the point of the inner blue cone of your Bunsen flame. While it is heating weigh out another fragment of about the same size and which will go into the neck of your 100-c.c. flask.

Fit up now the 100-c.c. flask with a drying-tube (beads and strong sulphuric acid). No delivery-tube is necessary. Put into the flask about 50 c.c. dilute HCl (1 part acid to 4 parts water). Wipe clean and dry. Place the apparatus in the balance-pan with the marble beside it. Counterpoise accurately.

Take out the stopper of the flask, drop in the marble; at once restore the stopper. When the fragment is completely gone, remove the stopper of flask and drying-tube for a few minutes; then put them in place, wipe clean and dry once more, and hang on the balance. Note carefully the weight change. What has caused this change?

2. After the first lump of marble has been heated in the flame for about twenty minutes remove it carefully, cool it, and take its weight. Compare the loss with that observed in (1). Note its appearance as compared with the appearance before heating. Break off a piece and try its solubility in water (test with litmus), also try (with another piece) the action of dilute nitric or hydrochloric acid. Next treat an unweighed fragment of marble in a small flask with dilute acid and bubble the gas through a little of the solution obtained by treating the *heated* marble with water.

Put a little marble *powder* in a piece of hard-glass tubing sealed at one end. Wrap the part of the tube where the marble is with a thickness of copper gauze, adapt a small delivery-tube dipping under the surface of some of the same solution used in the last experiment. Heat the upper portions of the marble as hot as possible with a good Bunsen flame. The temperature is considerably lower than when the marble was heated before and the effect may be less marked, but it will be enough to note and to compare with the results of the last experiment. What can you get from a study of your experimental work up to this point?

Set another weighed piece of marble heating in the flame as before; while it is heating the following experiments can be carried on:

Take about 50 c.c. lime-water in a wide-mouthed bottle. Bubble carbonic dioxide through it for a few minutes until considerable precipitate has formed. Filter, and try the behavior of the precipitate with acids. What evidence have you of its composition? With the results of this experiment in mind, take another 50 c.c. of lime-water and pass carbonic dioxide through it for some time after the precipitate appears. What happens? Filter (if the solution is not perfectly clear), and heat the filtered solution slowly to boiling, noting carefully everything that takes place.

What facts have been brought to light?

Return now to the lump of lime which has probably been heated long enough. Cool and weigh it. Next make a solution of about 5 grams dry sodic carbonate in about 15 c.c. of water. Drop the lump of heated marble into this solution. Heat to boiling for a few minutes.

Filter, taking care to wash *all* the solid on to the filter-paper. Wash the precipitate with water thoroughly (six or seven times) then dry the paper and precipitate thoroughly over a radiator or register. When *perfectly* dry place the filter-paper with its contents in one pan of the balance. In the other pan put a similar filter-paper to counterpoise the one containing the precipitate. Ascertain now the weight of precipitate and compare it with the weight of the marble *before it was heated.* Also try its action with acids. What are your results?

The substance obtained when any form of calcic carbonate is strongly heated is *calcic oxide.* It is called *lime,* or sometimes *quicklime* or *unslaked lime.* It is made in enormous quantities, as we shall soon see.

Weigh carefully about 1.5 grams good, white quicklime in a porcelain crucible. (If you have time to make it yourself from marble so much the better, as the material will be purer.) Moisten it with a few drops of water. Allow it to stand for a few minutes. Note carefully all effects. When the whole has crumbled away, set the crucible in the mouth of a 250- or 500-c.c. flask in which water is boiling. The steam will dry the material in the crucible and drive off extra water. Dry to constant weight. With how much water has each gram of calcic oxide united? With how many molecules of water has each molecule of calcic oxide united?

Approximate Atomic Weight of Calcium and its Replacing Power.—The best way for us to get at this point will be by an analysis of the chloride of calcium.

Place in one pan of your balance a beaker containing about 20 c.c. of distilled water. Counterpoise. Then drop into the beaker enough anhydrous calcic chloride to make from 0.2 to 0.3 gram. Ascertain the exact weight taken. Stir until all is dissolved; then add a concentrated solution of argentic nitrate until no more argentic chloride is produced on addition of another drop of the nitrate. Stir the solution quite briskly, when the precipitate should settle rapidly, leaving the liquid overhead almost perfectly clear. Pour the whole on a filter, washing every trace of the precipitate into the paper by a jet of water from your wash-bottle. Wash the precipitate thoroughly seven or eight times, taking care to begin the washing at the top of the paper each time. Dry the paper with adhering precipitate *in the funnel* over a steam-radiator or a hot-air register. When it is thoroughly dry carefully open out the filter on a piece of smooth paper and transfer the precipitate to a weighed porcelain crucible. Almost none remains sticking to the paper if the work is done carefully. Now support the crucible on a pipe-clay triangle and cautiously heat until the precipitate just barely begins to show signs of melting around the edges. Then cool and weigh. This gives us the weight of argentic chloride, and this same argentic chloride contains *all the chlorine that was formerly united with calcium.* Now it has been found by numerous experiments that argentic chloride contains very nearly 24.7% chlorine. If, therefore, we multiply the amount of argentic chloride weighed by 0.247, we shall get the amount of chlorine contained in the calcic chloride we have analyzed. Calculate, now, the atomic weight of calcium on the assumption that calcic chloride has the simplest possible formula ($CaCl$), taking the atomic weight of chlorine as 35.5.

The specific heat of such samples of metallic calcium as have been experimented upon is 0.1704. What does this indicate as to the formula you assumed for the calcic chloride, and what now appears to be the atomic weight of calcium? What is its replacing power (valence)? Write now the formula of its oxide; carbonate, sulphate, phosphate, hydroxide, and chloride.

See if you can express by suitable equations what takes place

(*a*) When calcic carbonate is heated;
(*b*) When calcic oxide is treated with water;
(*c*) When calcic carbonate is acted upon by nitric acid.

Keep carefully before you the results of your past experiments. They will be useful both qualitatively and quantitatively in making out the above reactions.

Such atomic weight determinations as this merely result in fixing the atomic weight of an element within rather narrow limits. They must be carefully distinguished from the elaborate and painstaking investigation by which the *exact* values are fixed. Such investigations extend sometimes through several years, and always involve months of very careful work. The main difficulty is found in selecting suitable compounds to analyze and in getting them pure.

Calcic Sulphate.—The naturally occurring form is called *gypsum*. It contains crystal water. In order to find out how much, weigh out 1 gram of gypsum in your porcelain crucible and heat to constant weight. Calculate from your results the number of molecules of crystal water present for every molecule of calcic sulphate.

Shake some powdered gypsum with water, filter, evaporate a few drops on a watch-glass. Has any dissolved? Add a few drops of the filtered solution to a solution of baric chloride. What result? Next heat the remainder of the filtered gypsum solution nearly to boiling. What happens? What facts are brought out by these experiments?

Calcic Chloride.—Expose some fragments of "fused calcic chloride" to the air for some time and note the effect. Dissolve some of the fused salt in water. Is the solution perfectly clear? Test it with litmus (first filter if necessary). Dissolve some more. Add a little hydrochloric acid. Then add finely-powdered marble and boil the solution for a while, keeping up the bulk by occasionally adding a little water. Filter and test the solution with litmus. Evaporate a small portion of the solution to dryness in a porcelain dish. Cool. Treat the residue with water. Test with litmus.

LECTURE 49.

WE are now in a position to understand the conditions under which calcic carbonate is dissolved by water. Water sinking under the soil meets and dissolves carbonic dioxide, which is constantly given off from decaying vegetable matter. We have seen that water in which carbonic dioxide is dissolved has the power of dissolving calcic carbonate. Moreover, the water is often exposed to considerable pressure in its travels under the earth's surface. Under these circumstances it dissolves more carbonic dioxide than it would at ordinary pressure, and the power of dissolving calcic carbonate increases proportionately. When such a water comes to the surface as a spring or drips from the roof of a limestone cave, it loses part of its gas and consequently part of the calcic carbonate it contains. According to conditions this may result in the slow formation of an extensive sediment or it may result in the formation of a stalactite.

Waters thus saturated with calcic carbonate, or, in general, waters containing calcium or magnesium salts, are called *hard waters*. They are inconvenient, because the soaps react with the calcic carbonate, forming *calcium soaps*, which are sticky and not very soluble. Such waters can sometimes be "softened" by boiling, when the extra calcic carbonate is precipitated as a whitish mud. We shall return to this point again in another connection.

When limestone is heated to whiteness it forms "lime." This process of "burning" limestone (as it is commonly called) is carried out in huge iron or fire-brick furnaces or *kilns*, into which the limestone and fuel are charged, the burned lime being occasionally drawn off at the bottom, through an opening provided for the purpose.

When lime is treated with water it combines with it so energetically that the heat evolved usually causes the water to boil. This operation is called *slaking*, and the product (calcic hydroxide) is called *slaked lime*. This substance mixed with good, sharp sand makes *mortar* with which houses are plastered. When this mortar is allowed to stand it gradually hardens, and the hardening goes on for years. During the process of hardening, tests show that the calcic hydroxide changes partially to calcic carbonate, and this change is probably responsible for the hardening, the calcic carbonate cementing the whole together. Calcic carbonate often acts this way. For instance, many of the natural "*sandstones*" consist simply of grains of sand cemented together by calcic carbonate. When treated with dilute acids the calcic carbonate is decomposed and the sand is untouched, so the sandstone simply crumbles away to a mass of sand.

Some limestones are quite impure—so impure that the lime made from them contains anywhere from 10 to 30% impurities. The most frequent impurity consists of *silicates* of certain metals, principally aluminum, calcium, iron, and potassium. These silicates are mostly salts of *silicic acid*, whose formula is just like that of carbonic acid, only with the element *silicon* in place of carbon (H_2SiO_3). A very large proportion of the rocks of the earth's surface are salts of this acid.

Some of these impure limestones are very remarkable, and very useful, from the fact that when mixed to a thick paste with water they harden *even when under water*, and hence when they are mixed with sand and water, they form a kind of mortar which can be used for masonry which has to stand the action of water. The mortars or *cements* thus made are called *hydraulic cements*, and are of very great value. Most of those now on the market are made artificially by mixing suitable proportions of limestone and clay, "burning" the mixture and grinding it fine; but some are made from a rock which contains the right mixture to start with, and is simply "burnt," ground, and barreled. *Concrete* is simply a mixture of some good hydraulic cement with sand and broken stone, or beach gravel. It sets to a perfectly solid mass; and is used in building the foundations of bridge-piers, etc.

Calcic sulphate, or *gypsum*, is found in nature in several forms. *Selenite* looks much like mica, but is more brittle and is easily scratched by the thumb-nail. *Satin spar* would almost be recognized by its name. It usually consists of a mass of snow-white, parallel, closely-packed crystals, which are exceedingly slender and threadlike and give a satiny look to the mineral. It is very soft, like selenite. *Massive gypsum* is blasted out in large rough fragments, in which no distinct individual crystals can be seen.

It carries crystal water (how much?), which it gives up when moderately heated. *Plaster of Paris* is simply gypsum, which has been heated to a temperature of about 200° to drive off its water. It is a white powder. When mixed with water it takes back its crystal water with quite a decided rise of temperature, and sets into a hard mass. This hardening is attended with *expansion*. These facts make plaster of Paris a very useful substance for making casts or impressions of statuary, coins, or medallions; since in the act of setting it expands, forcing itself into every minute line of the mould.

Burnt gypsum is also used in kalsomining, and in the manufacture of fertilizers.

Calcic chloride, when deprived of part or the whole of its six molecules of crystal water, is used in drying gases.

Calcic Phosphate occurs in nature crystallized as *apatite* in bluish-green, hexagonal crystals, also in large deposits in the Southern States in the form of pebble and rock deposits. Its main use is in the manufacture of fertilizers. The phosphates have to be furnished the growing plant in soluble form. Calcic phosphate is difficultly soluble. In order to convert it into a soluble form, it is treated with concentrated sulphuric acid, which acts thus:

$$Ca_3(PO_4)_2 + 2H_2SO = CaH_4(PO_4)_2 + 2CaSO_4$$

The mixture of acid calcic phosphate and calcic sulphate is called *superphosphate of lime*, and forms the basis of most fertilizers.

Other Elements resembling Calcium.—Strontium and barium are very much like calcium: but their compounds are not so important. The only strontium salt that is of much use is the nitrate, which is used in making red fire. Strontium salts color a flame bright crimson.

Some barium salts, such as the chloride and carbonate, are used in the laboratory, but there are few other compounds of any importance.

The compounds of barium and strontium are very widely distributed in nature, but as a rule in small amounts. They are found in traces in practically all naturally-occurring forms of calcic carbonate, and can be detected in the ashes of many plants, in egg-shells, and in the shells of oysters, clams, etc.

The spectroscope constitutes the most delicate means of distinguishing these three elements. They can, however, be recognized simply by the color and behavior of the Bunsen flame when one of the salts is brought into it. Barium compounds give a greenish-yellow flame, strontium a bright crimson one, and calcium a dull-crimson one, which flickers and only remains for a few seconds, but reappears on moistening the wire with hydrochloric acid and heating again.

Considered as a group, these elements are noteworthy. The following table sets forth some of the most interesting points. It will be seen that as the atomic weights rise there is very commonly a regular gradation in the properties of the elements and their compounds.

Metal.	Atomic Wt.	Sp. Gr.	Sulphate.	Carbonate.	Hydroxide.
Calcium, Ca	40	1.85	Somewhat soluble in water.	Practically insoluble.	Slightly soluble in water.
Strontium, Sr.	87.5	2.5(?)	Less soluble.	More soluble.	More soluble.
Barium, Ba.......	137.5	3.75(?)	Practically insoluble.	Somewhat soluble.	Easily soluble (hot water.)

They are well defined and typical *elements*, as well defined as any we have had to do with, and from the fact that they yield white "earthy" oxides which react more or less with water, forming sparingly-soluble hydroxides whose solutions are alkaline, they have been called the *metals of the alkaline earths*.

GLASS.

There is a certain acid called *silicic acid*, whose salts are very abundant in nature, and are notable from the fact that they are, with very few exceptions, very difficultly soluble in water. For that matter, most of them are difficulty soluble in acids. These salts are derived from acids called the silicic acids, the simplest one of which has the formula H_2SiO_3. Its salts are in formula like the carbonates, only with the element silicon instead of carbon.

Common white sand (which is mostly quartz) is the oxide of silicon (SiO_2) and bears the same relation to silicic acid (H_2SiO_3) that carbonic dioxide, CO_2, does to carbonic acid, H_2CO_3, and just as CO_2 acts upon the strong metallic hydroxides to form carbonates, so when silicic dioxide, SiO_2, is melted with alkalies, it forms *silicates*. The different forms of *glass* consist of mixtures of various metallic silicates, and the process of making glass consists in melting down mixtures of sand with lime and with sodic carbonate or potassic carbonate, according to what kind of glass is wanted. The melting temperature has to be exceedingly high, for glass does not melt sharply, but slowly softens, passes through an intermediate pasty stage, and finally becomes fluid as water. When it cool it passes through the same stages in reverse order.

The main materials actually used in making common window-glass are clean white sand, "soda-ash" or sodic carbonate, and lime. The melting is done in large, peculiar-shaped fire-clay pots. The materials almost always contain some iron compounds in small quantities as impurities. These iron compounds would color the glass a yellowish-green or brownish-green, according to the quantity present. As this is undesirable, the tendency is corrected by adding to the charge a small quantity of *manganese dioxide*. This substance when melted into glass colors it pink. The pink color is the *complementary color* to the yellowish-green, and the result is that the two effects neutralize each other and the glass appears colorless. The charge when melted down may be treated in one of two ways, assuming that it is for window-glass: (1) It may be blown into long, cylinder-shaped bulbs, such as shown in Fig. 48. The ends of the bulb are cracked off, the whole cylinder is cut down the middle and laid *cut uppermost* on a smooth, hot, iron plate, where it slowly opens and spreads out to a large sheet, which is then cut into the various sizes required. (2) The melted glass, instead of being blown, may be emptied bodily out into a smooth, iron plate, rolled out into a sheet of the required thickness by heavy rollers while it is still hot and soft, and finally ground and polished. The product thus obtained is called plate glass. It is clearer than common glass, but is decidedly more expensive.

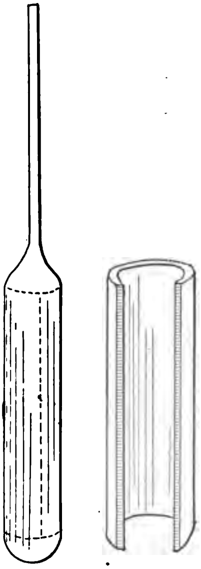

FIG. 48.

In making the celebrated Bohemian glass very pure sand, marble, and potassic carbonate are used. This glass is white, hard, difficult to melt, and resists the action of acids and most other reagents. Most laboratory glass articles are made from Bohemian glass.

By substituting lead oxide for lime,—that is by making a mixture of lead, oxide potassic, carbonate and sand,—we get a *lead glass* or *flint glass*. This is a very heavy form of glass. It is rather more easily attacked by reagents than are the other varieties. Flint glass is used in making lenses, prisms, etc., for optical instruments. Its use for these purposes depends upon the fact that it refracts light more powerfully than do the other forms. *Cut-glass* is simply a very white, brilliant glass, into which various figures or lines have been *cut* or ground by revolving wheels having sharp wedge-shaped edges and fed with sand or emery. After the figures are ground in they are polished.

When glass lies buried in the earth for a long time it is attacked by water and other substances in the soil, with the result that a very thin layer on its surface is changed in composition. This little film makes the glass show a constant play of rainbow colors. This effect is now produced artificially by heating the glass articles with strong hydrochloric acid under pressure.

The oxides of many of the metals color glass when they are melted in with it. Some of the colors are given below:

Cobalt oxide,	blue.
Chromium oxide,	green.
Gold,	red.
Manganese oxide,	amethyst color.

LECTURE 50.

MAGNESIUM—ZINC—(CADMIUM)—MERCURY.*

UP to this time in our studies of individual elements we have found it possible to deal with a single element as a representative of a group, and the relationship between different members of the same group, or family, has been clear and decided. The four elements named above bring us a little perplexity, for while they have a number of things in common, some of them have also considerable in common with elements of other groups; so much that some chemists would not consider these four metals together as we are to do, but would study some of them in other connections. The fact is that the classification of the elements and the right understanding of their relations to each other is to-day in a rather incomplete state at best. It will, however, help us to a sense of the situation if we look for a moment at what has been attempted and done in this direction.

The beginning was in 1817, when Döbereiner pointed out that it was, to a certain extent, possible to study the elements in groups of three or *triads*. In most cases these groups consisted of elements which had very obvious resemblances and relationships to each other. For example, we should study sodium, potassium, and lithium together, independently of any idea of classification, simply following out the plain *fact* that they are remarkably alike in a great many ways. The same is true of calcium, strontium, and barium; of sulphur, selenium, and tellurium; of chlorine, bromine and iodine, and several other groups of three. But Döbereiner also pointed out that the atomic weights of the members of such a *triad* showed a curious relationship. Look, for instance, at those given below:

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* See Venable, "The Periodic Law."

Lithium	7	Calcium	40	Sulphur	32
Sodium	23	Strontium	87.5	Selenium	78.9
Potassium	39	Barium	137.5	Tellurium	125

Phosphorus	31	Chlorine	35.5
Arsenic	75	Bromine	80
Antimony	120	Iodine	126.5

In each case the middle element has an atomic weight which is very closely the arithmetical mean between the other two.* This is not a mere matter of numbers, though. Consider for a moment the group we have just been studying. Without any reference to atomic weights or classification we should naturally put calcium, strontium, and barium not only in the same group but in this order, strontium coming between calcium and barium, because, *as a matter of fact*, strontium in all its physical and chemical behavior lies between the other two. For example, the specific gravity of metallic strontium lies between that of calcium and barium; and the same is true of the melting-point and specific heat. Strontic hydroxide is more soluble in water than calcic hydroxide, but not so soluble as baric hydroxide. Calcic chloride absorbs moisture from the air eagerly; strontic chloride does also, through to a considerably less extent; and baric chloride not at all.† Calcic sulphate is somewhat soluble in water; Strontic sulphate less so; and baric sulphate almost insoluble. We should encounter the same thing in dealing with other groups.

Döbereiner's remarks on this subject did not attract much attention. One very good reason was, that the whole matter of atomic weights was in an unsettled and unsatisfactory state; and the foremost chemists of the time were not disposed to attach much importance to relations between numbers whose values were so insecurely fixed.

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* The atomic weights here used are rounded off in the decimals.

† These statements refer to the salts with two molecules of crystal-water.

The renowned French chemist, Dumas, took up the matter again in 1851 and aroused much interest in the subject, especially as he had done a great deal to straighten out the matter of atomic weights. From then on we find in the literature of the subject clear indications of an idea gradually forming itself in the minds of thoughtful men, that this classification into *triads* was only fragmentary, and that the elements as a whole were capable of a classification, which would include the triads and at the same time give a broader and clearer view of the relations between the elements. One of the main facts which led men to look for a larger classification was that strong resemblances often exist between elements of different groups—that is, there is a relation between *groups* as well as between the individual members of each group.

The crystallization of this thought began in 1862. Between that date and 1871 appeared publications by four writers, all of whom had worked out what they presented practically independently of each other. The order in which the names appear as to time is given below:

A. E. B. De Chancourtois	(French)	1862
J. A. R. Newlands	(English)	1863
D. Mendeléeff	(Russian)	1869
L. Meyer	(German)	1870

It is curious to notice that the same idea was worked out in four different countries. There is considerable dispute to-day as to how the credit for the discovery should be distributed; but there is no doubt as to which name is the most prominently and justly associated with the clear statement and the development of what is now regarded as a great law of nature. That honor belongs to Mendeléeff; and the fact which he not only perceived but stated clearly is that *if the elements be arranged according to the magnitude of their atomic weights their properties do not always change uniformly as the atomic weights rise, but alternately rise and fall in intensity.* The original statement was more concise, but means the same thing. "The elements, if arranged in the order of their atomic weights, show a very evident *periodicity* of properties."

To make this point clear, let us arrange the first eighteen elements in the order of their atomic weights:

Lithium	Beryllium	Boron	Carbon	Nitrogen	Oxygen	Fluorine
7	9.2	11	12	14	16	19
Sodium	Magnesium	Aluminum	Silicon	Phosphorus	Sulphur	Chlorine
23	24	27	28	31	32	35.5
Potassium	Calcium	Scandium	Titanium	Vanadium	Chromium	Manganese
39	40	44	48	51.1	52.3	55.

As our first basis of comparison let us consider the combining power toward oxygen, that is, the formula of the highest oxide each element can form. The compounds are:

Li_2O	BeO	B_2O_3	CO_2	N_2O_5	——*	——
Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
K_2O	CaO	Sc_2O_3	TiO_2	V_2O_5	CrO_3	Mn_2O_7

It will be seen that this power increases through seven elements and then drops back where it started from. The same thing is repeated through a second seven, and so on. Other properties, physical and chemical show, the same tendency. Now if we arrange these rows of seven elements under each other so that the eighth element comes directly under the first, the fifteenth under the eighth and first, and so on, *we obtain a table in which we find elements of like properties arranged in vertical rows.* Such a table is given on the opposite page.

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* Fluorine forms no oxygen compounds at all.

SERIES.	GROUP I. — R_2O.	GROUP II. — RO.	GROUP III. — R_2O_3.	GROUP IV. RH_4. RO_2.	GROUP V. RH_3. R_2O_5.	GROUP VI. RH_2. RO_3.	GROUP VII. RH. R_2O_7.	GROUP VIII. — RO_4.
1	H = 1							
2	Li = 7	Gl = 9	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27	Si = 28	P = 31	S = 32	Cl = 35.4	Fe = 56, Co = 58.7, Ni = 58.6.
4	K = 39	Ca = 40	Sc = 44	Ti = 48	V = 51.1	Cr = 52.3	Mn = 55	
5	(Cu) = 63.2	Zn = 65	Ga = 69.9	Ge = 72.3	As = 75	Se = 79	Br = 80	Ru = 103.5, Rh = 104.1, Pd = 106.2.
6	Rb = 85	Sr = 87.5	Y = 89	Zr = 90.4	Cb = 93.7	Mo = 95.9	— = 100	
7	(Ag) = 108	Cd = 112	In = 113.7	Sn = 118	Sb = 120	Te = 125	I = 127	
8	Cs = 133	Ba = 137	La = 138.5	Ce = 141.5	Di = 145	—	—	— — —
9	(—)	—	—	—	—	—	—	Os = 191, Ir = 192.5, Pt = 194.3.
10	—	E = 166	Yt = 173.2	—	Ta = 182	W = 184	—	
11	(Au) = 196.7	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
12	—	—	—	Th = 232	—	U = 240	—	— — —

For example: in group I. come lithium, sodium, potassium, rubidium, and cæsium, which we have already studied. In the same group fall copper, silver, and gold, whose resemblance to the metals thus named does not seem at first sight very clear. They present some features which seem to put them in a sort of sub-group by themselves. In fact, each group shows the same feature, and this has been emphasized in the table by setting off a little to the right those elements which have marked relationships among themselves, which distinguish them from the rest of the group. For example, in the second group come calcium, strontium, and barium, thus appearing as close relatives as they should; but in the same group come magnesium, zinc, cadmium, and mercury, and these are set off to the right because on the whole they constitute a sort of sub-family by themselves, though with regard to magnesium it is more or less of a balance, as we shall soon see.

It will be noticed further, that the numerical difference on passing from one atomic weight to the next at the right is generally small. In some places we find decidedly larger differences; and this *may* mean that the elements which should naturally come in there are not as yet known. Such breaks are indicated by blanks in the table.

These blanks have given rise to much speculation, some of which has led to investigations and results. So regular is the periodic variation of the properties, chemical and physical, that it has proved possible to predict approximately not only the atomic weights of the element which would belong in a given blank space, but also to predict its physical and chemical properties. Several such predictions were made by Mendeléeff, and his predictions led to investigations resulting in the discovery of elements which accorded in a most remarkable manner with the predicted ones.

Further consideration of the table at this time would take take us too far afield. For us its main interest is that it helps us keep in mind relationships between elements, and thus assists us in our study.

It has not been thought best, thus far, to attempt to study the elements in the strict order in which the groups come. Our object has been to take them in such order as seemed likely to render clear and emphasize the particular points under discussion. We shall continue this policy with the help of the Mendeléeff table, only it must be remembered that such a table has to be used with good judgment, and in such elementary studies as we are now pursuing it will not be wise to spend too much time in studying relationships unless they stand out pretty distinctly. We shall find that some of the groups indicated to us by the table will be less decided in this particular than others. The one now under consideration is an excellent example of such a group. And we will study it particularly from this point of view. It shows some peculiarities which our other groups have only shown very faintly.

It will be best to begin our study of these elements in the laboratory, though we are already familiar with some points in their chemistry.

LABORATORY WORK.

The first point to be brought out is that magnesium has some decidedly strong relations to calcium, strontium, and barium. For example, neither zinc nor mercury * decompose water except at high temperatures. Magnesium will decompose it *slowly* at 100° and more rapidly as temperature rises. Saturate half a test-tube full of water with fused calcic chloride. This solution has a high boiling-point, and when heated to boiling will behave toward metallic magnesium just as water would, only more strongly on account of the higher temperature. Pour the solution into your 100-c.c. flask, add about half a gram of magnesium (ribbon or powder, whichever happens to be most convenient).

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* Cadmium, being a comparatively rare element, will not be considered.

Fit a cork and delivery-tube to the flask and arrange to collect any gas that may come off. Heat the solution to gentle boiling for some minutes, and collect in the usual manner any gas that comes off. Satisfy yourself what the gas is. Has the magnesium undergone any perceptible change? Filter the solution, and cork it up for future use. Dry and return the magnesium to the bottle, if any is left unchanged.

Secondly, magnesic oxide resembles calcic oxide more than it does the oxides of the other metals of its own group:

1. Place a little on a piece of moist litmus-paper. Try the same with zinc oxide and with mercuric oxide.

2. Weigh out in a porcelain crucible about ½ gram magnesic oxide. Moisten it with water; allow it to stand for some hours, keeping it moist. Dry off the excess of water over a radiator or register. (Dry until the weight is constant.) Is there any increase in weight?

3. Magnesic carbonate is much like calcic carbonate, only it is more easily decomposed by heat.

Weigh out about 2 grams magnesic carbonate* into your small heating-tube of hard glass. Arrange to pass the escaping gas through "lime-water." Heat the tube containing the magnesic carbonate and note how much more rapid the evolution of gas than in case of calcic carbonate.

Next we come to some points in which magnesium is more like zinc:

1. To a solution of calcic chloride add a solution of ammonic sulphate, or sodic sulphate. Do the same with a solution of magnesic chloride. What difference appears? Does zinc form a soluble or an insoluble sulphate? What evidence have you to offer?

2. Evaporate a little calcic chloride solution (about 10 c.c.) to complete dryness in a small porcelain dish. Test the steam with litmus frequently, heating the bottom of the dish pretty hot. Finally cool and treat the residue with about 20 c.c. water. Does the residue dissolve readily in water? Repeat the experiment with 10 c.c. of magnesic chloride solution. Do any differences appear? Try the same with 10 c.c. zincic chloride solution. Sum up now the points in which magnesium is like calcium, and those in which it is like zinc.

* Use the naturally occurring magnesic carbonate (which is called *magnesite*), if is available.

Mercury.—Try the action of hot, dilute hydrochloric, sulphuric, and nitric acids (in the order named) upon a globule of mercury the size of a match head. Compare it with zinc and magnesium in this regard. (In case of magnesium use only very small fragments.) Try now the same thing exactly with small fragments of copper and silver. Which group do these come in? Which group does mercury most resemble thus far?

The fact is, the resemblances between zinc and mercury are not at all apparent; and it is often thought best to study it in connection with copper and silver, which it resembles decidedly in its chemical behavior. The main interesting feature about mercury for us is brought out by the following experiments:

1. Gently heat a globule of mercury the size of a pea with about 2 c.c. dilute nitric acid mixed with its own bulk of water. Warm gently until all action is at an end. Carefully pour off the solution into another test-tube and divide it into two parts, *A* and *B*. Dilute *A* somewhat and divide it into three portions. To one portion add sodic hydroxide; to another potassic iodide solution (KI); and to the third, hydrochloric acid. Note carefully the colors and characteristics of the precipitates.

To *B* add a few drops of concentrated nitric acid, and boil. Then dilute, and divide it into three parts, as in case of *A*, and make the same experiments.

Sum up your results now. In stating them be careful how you attempt to draw conclusions. Keep to the facts, and content yourself with stating them fully and clearly.

Tests for the Presence of Magnesium and Zinc.—Zinc and magnesium compounds may be recognized by their behavior when heated intensely with cobaltous nitrate. Any zinc compound thus heated yields a green mass on cooling. Any magnesium compound yields a light-pink mass.

The substance to be tested is first heated as hot as possible on charcoal by the blowpipe flame. It is then cooled, moistened with a drop of cobaltous nitrate solution, and heated again. After cooling the color is observed.

If the substance to be tested is a solution, it may be concentrated by evaporation, and the concentrated solution soaked up with a wad of filter-paper which is then treated as above.

Test for the Presence of Mercury.—Dissolve the substance in as little nitric acid as possible (adding perhaps a drop of hydrochloric acid to hasten the action). Evaporate to small bulk to get rid of part of the acid; then add a little water and a bright fragment of copper wire. The copper turns silver-white, from the metallic mercury which is deposited on it. The coating can be volatilized by heating the wire. Silver also separates as a white metallic film on copper under these circumstances, but the coating is not volatile.

Amalgams.—Place a small pea of mercury in an evaporating-dish and just cover it with dilute sulphuric acid. Stir round in it clean, bright fragments of

1. Iron (bright wire).
2. Silver (small fragment of sheet silver or wire).
3. Copper (use a cent, or a piece of wire).
4. Lead.
5. Tin.
6. Aluminum.
7. Magnesium (ribbon. Wash the mercury free from acid before trying this. Why?).

Take a solution of mercuric chloride containing a little free hydrochloric acid. Dip into it successively clean fragments of the same metals experimented with above.

LECTURE 51.

METALLIC magnesium is prepared by heating magnesic chloride with sodium. It is a white metal with a high lustre and comparatively little tarnished by ordinarily dry air. Its specific gravity is 1.74. It is one of the lightest known metals. It can be rolled into thin ribbon or reduced to powder, and is sold in both forms. The powder is mainly used (mixed with potassic chlorate) in photography for taking "flash-light" pictures, for the light emitted by burning magnesium affects the salts of silver which are used in photography in the same way as sunlight does. It is very rapidly attacked by acids. When brought into the strong acids the action is very violent and often accompanied by a flash of light.

Magnesic oxide is known in commerce as *magnesia.* It is a pure white, light powder which is usually made by heating magnesic carbonate. It is used in medicine somewhat and is a constituent of most of the so-called "toilet-powders."

Magnesic sulphate is known as *Epsom salts.* It is a white, crystalline salt which is found in certain mineral waters. It is obtained as a by-product in manufacture of common alum, and is used in medicine as well as in the manufacture of cotton goods. It has also some value as a fertilizer (compare with calcic sulphate). It carries seven molecules of crystal-water. On heating, six of these go off quite easily: the last is expelled with much more difficulty.

Magnesic chloride may be made by dissolving the carbonate in hydrochloric acid. When, however, the solution is evaporated to dryness the chloride is mostly *decomposed by the water-vapor.* Hydrochloric acid is given off and *the oxide* remains.

This is the first glimpse we have had of something we shall frequently see hereafter—namely that the salts of any except the strongest and most decidedly metallic elements are apt to be more or less affected by water, either when they are simply dissolved in it or when their water solutions are evaporated. This is, as we shall presently see, the reason why most salts react slightly acid in water solution. The action which takes place in the present case may be represented thus:

$$MgCl_2 + H_2O = 2HCl + MgO.$$

Naturally Occurring Magnesium Compounds.—*Magnesite* is magnesic carbonate, a white compact mineral. *Soapstone* and *meerschaum* are silicates of magnesium. *Asbestos* is a silicate of magnesium and other metals.

ZINC

is a metal of great commercial importance. It is not found in nature in the free state, but some of its compounds are fairly abundant in certain localities, and from these compounds or *ores* * the metal is extracted. The principal ones are, *sphalerite* or *blende*, which is zincic sulphide; *calamine*, a silicate of zinc, and *Franklinite* (Franklin, N. J.), a compound of iron, zinc, and oxygen.

In the preparation of the metal, the ores are first heated in contact with the air, which results in the oxide being finally obtained. The sulphide undergoes the following change under such treatment:

$$2ZnS + 3O_2 = 2ZnO + 2SO_2;$$

that is, the sulphur and the metal are simultaneously oxidized, the sulphur going off as SO_2. Next the oxide is "reduced" to metal by heating it to a high temperature with charcoal or coal-powder. The retorts in which this is done are built into the wall of a furnace with the open ends outward and to these necks are attached iron receivers. The zinc is raked out of the receivers from time to time as the reduction goes on.

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* An *ore* of a metal is a compound which occurs in sufficient abundance and is of such texture and composition that the metal may be extracted from it on a large scale at a money profit.

The metal is bluish-white in color and very lustrous. At ordinary temperatures it is rather brittle. At 100°—150° it can be rolled into sheets. When heated to a high temperature in the air or in oxygen it takes fire and burns with a very characteristic bluish flame. When clean sheet-iron is drawn through a tank of melted zinc, the zinc adheres to it and forms a very beautiful "frosted" coating composed of crystalline zinc. This surface tarnishes only slowly, and iron is, therefore, often treated in this way. The process is called *galvanizing*. Wire is similarly treated. When zinc and copper are melted together they give a yellow *alloy* called *brass*.

It is dissolved by all the dilute acids. With hydrochloric acid and sulphuric acid hydrogen is given off. The action of nitric acid is more complicated, lower oxides of nitrogen like N_2O and ammonia being among the products. *It is also slowly dissolved by boiling sodic hydroxide and potassic hydroxide, with evolution of hydrogen.* The solution contains a compound of zinc, oxygen, and sodium or potassium, as can be shown by adding alcohol to the solution, when a compound having the above composition is precipitated. This substance when dissolved in water does not act like a zinc-salt, but like a potassium-salt or sodium-salt. It does not give the ordinary precipitates yielded by zinc solutions. The only view that seems sensible is that the zinc in presence of the strong alkalies *assumes temporarily the part of a non-metal or acid-former*, and that the salts above mentioned are *sodium or potassium zincates*, the simplest ones having the formula Na_2ZnO_2 and K_2ZnO_2.

The same compounds are obtained when zincic hydroxide is dissolved in sodic or potassic hydroxide. Toward the acids, then, zincic hydroxide acts like any ordinary basic hydroxide, while toward the alkalies it acts as a weak acid; thus,

$$\begin{aligned} Zn(OH)_2 + 2KOH &= K_2ZnO_2 + 2H_2O, \\ Zn(OH)_2 + 2HCl &= ZnCl_2 \quad + 2H_2O. \end{aligned}$$

This is the first instance of the kind that has come under our notice, but it will not be the last by any means, for such behavior is not uncommon. Metals which manifest it do not generally form well-defined and stable salts, and their salts with the strong acids usually react acid. In the present case this is conspicuously true. The chloride, sulphate, and nitrate of zinc all react acid in water solution. We will consider this matter in connection with zincic chloride.

Zincic oxide is made by burning zinc in the air or by heating the nitrate, carbonate, or hydroxide. It is white, and when ground with oil is used as a paint under the name of "zinc-white." It is not blackened by hydrogen sulphide *because zincic sulphide is white.* Common white paint is substantially a lead carbonate ground in oil, and since the sulphide of lead is black the paint is easily discolored by hydrogen sulphide.

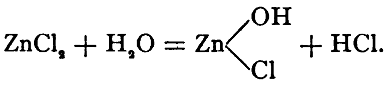
Zincic sulphate is obtained by dissolving the metal or the oxide in dilute sulphuric acid. The crystals which separate on evaporating the solution are white and needle-like. They contain seven molecules of crystal-water, and are in many ways very much like the crystals of magnesic sulphate. The salt is used in cotton printing and in medicine.

Zincic phosphate is used as a filling for teeth. It is prepared for this purpose by mixing zincic oxide and a syrupy solution of phosphoric acid. The mass "sets" rapidly to a hard, white mass.

Zincic Chloride.—This salt may be made either by the direct action of gaseous chlorine upon zinc or by dissolving the metal or its oxide, hydroxide, or carbonate in hydrochloric acid. On evaporating the solution there remains an oily residue which, when heated hotter, partly volatalizes and partly undergoes decomposition with formation of the oxide. When dissolved in water its solution is markedly acid.* From what we have seen of the non-metallic tendencies of zinc it is not surprising that it should, in its chloride, imitate somewhat the behavior of such chlorides as that of phosphorus or antimony toward water. In the case of antimony we have

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$

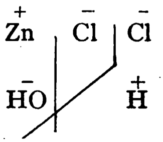
And in the case of zinc much the same thing appears to happen; perhaps thus:



$$ZnCl_2 + H_2O = Zn\begin{matrix}\diagup OH \\ \diagdown Cl\end{matrix} + HCl.$$

The zinc compound obtained is called a *basic chloride* of zinc. In the decomposition hydrochloric acid is formed, which accounts for the acidity. The dissociation theory explains this matter a little more completely.

The zincic chloride dissociates in water solution thus:



There are always present in water some few free hydrogen and hydroxyl ions, for water, as will be remembered, is dissociated to a very slight extent; and when the ions of water and the ions of zincic chloride meet in water there is the opportunity to form one of these basic chlorides, which are, as a rule, sparingly soluble, and are always very slightly dissociated. The effect of the formation of such a basic chloride is to take some of the hydroxyl ions from solution, leaving an excess of free hydrogen ions, which accounts for the acidity.

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* Neither litmus- nor turmeric-paper are admissible here, for a solution of zincic chloride turns red litmus slightly blue and blue litmus slightly red. The same is true of the turmeric colors. Phenol-phthalein acts normally.

Fused zincic chloride is used in surgery as a *caustic.* Its use for this purpose depends upon the fact that it absorbs water with great eagerness and will even remove the necessary hydrogen and oxygen from substances which contain no water *as such.* It acts, then, to destroy and disintegrate flesh.

Mercury is the only one of the common metals which is liquid at ordinary temperatures. It is principally obtained from one of its sulphides which has the formula HgS, and is a red crystalline mineral. On heating it the sulphur is oxidized to SO_2 and the mercury distils off and can be condensed. Sometimes pure mercury is found in drops enclosed in rocks or in the soil. It solidifies at $-39.5°$, and is closely 13.6 times as heavy as water. It is permanent in the air at ordinary temperatures. It is extensively used in thermometers, barometers, and in many other kinds of chemical and physical apparatus. It is also used in the extraction of gold and silver from their ores, and in making mirrors; these latter uses depending upon the power it possesses of dissolving the metals forming what are called *amalgams.* In many forms of galvanic batteries zinc is one of the metals employed. In order to keep the zinc from wasting too rapidly the surface is covered with a thin coating of mercury, which forms as amalgam with the zinc on the surface, and this solution of zinc in mercury is naturally more slowly attacked by acids than the unamalgamated zinc, just as sodium amalgam is less rapidly decomposed by water than is pure sodium. *The vapor of mercury is poisonous.*

COMPOUNDS OF MERCURY.

Mercury forms two distinct sets of salts and other compounds. In one set its replacing power is evidently *two*, in the other it is apparently *one*. Thus we have two chlorides, $HgCl$ and $HgCl_2$; two oxides, Hg_2O and HgO; two nitrates, $HgNO_3$ and $Hg(NO_3)_2$, and so on.

We distinguish them by calling the compounds in which the metal has the lower "valence" the *mercurous* compounds and the others the *mercuric* compounds. The mercurous compounds can be changed into the mercuric compounds by treatment with any reagent which *sets free oxygen in the solution*. Conversely the mercuric compounds can be changed into mercurous compounds by any mixture which acts as an absorber of oxygen.

The best way of getting a *mercurous* solution to serve as a starting-point in making mercurous compounds generally, is to heat dilute nitric acid with more mercury than it can dissolve. By boiling a portion of the solution with a little strong nitric acid (a good oxidizing agent) we can change it into mercuric nitrate.

Among the mercury compounds worthy of special mention we have first *mercuric oxide*, which is made by heating mercuric nitrate and which is the substance from which Priestly first obtained oxygen.

Mercurous chloride is used in medicine under the name of *calomel*. It is very difficultly soluble in water, and consequently can be made by precipitating any mercurous solution with a soluble chloride. It is also made by heating together mercury and *mercuric chloride*, which is made on the large scale by heating a mixture of mercuric sulphate and common salt, when the mercuric chloride volatilizes and is condensed. Mercuric chloride volatilizes without melting and condenses as a solid, or, as the term is, it *sublimes*. Its principal use is in dilute water solution as an *antiseptic* by physicians. This latter use arises from the fact that it acts as a poison to most organisms which are instrumental in decay, and toward disease germs. Any substance which acts thus is called an *antiseptic.* Antiseptic bandages are bandages which have been impregnated with mercuric chloride solution. Surgeons wash their hands and their instruments in a weak solution of mercuric chloride before and after performing any surgical operation. The commercial name of mercuric chloride is *corrosive sublimate.*

LECTURE 52.

BORON, ALUMINUM.

A GLANCE at the Mendeléeff table will show that the group headed by the two elements named above contains a number of others. They are, however, all rare, and we will not consider them here. Of the two selected for study, aluminum is in the main metallic or basic in its properties, while boron is for the most part acidic or non-metallic. Here, then, we are studying once more a group which contains both classes of elements.

The two elements themselves are not much alike in any way, and in fact their compounds, though they possess a few points of resemblance, are not strikingly similar. The fact is that the elements of lowest atomic weight in each group show, as a general rule, marked relationship with preceding and following groups, and the same is true at the other end of the line—that is, of the elements of highest atomic weight. For instance, lithium has some very decided points of resemblance to the calcium group. Mercury is about as much like silver and copper as it is like zinc and cadmium, and here the element boron in its appearance is more like carbon than anything else, while in its compounds it resembles aluminum and the rest of its own group somewhat, but is in some respects more like the nitrogen group.

Realizing, then, that in studying the leading element of a group we are always sure to meet difficulties like these, we may as will consider boron in its own group—that is, in connection with aluminum.

The atomic weight of boron is closely 11 and its valence is *three*. It forms only one oxide, B_2O_3, *boric oxide*, sometimes called *boron trioxide* and sometimes *boric anhydride*, because it is an acid-forming oxide, and when dissolved in water gives on evaporation of the solution crystals of *boric acid;* thus,

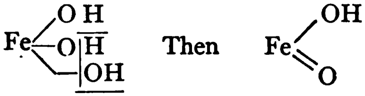
$$B_2O_3 + 3H_2O = 2H_3BO_3,$$

which is, as will be seen, an hydroxide of boron $B(OH)_3$. When neutralized by alkalies, salts are formed called *borates*, but these salts are as a rule unstable and need not be further considered.

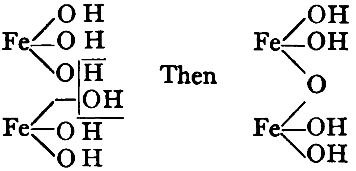
When a hot, strong solution of boric acid is neutralized with sodic carbonate, a salt crystallizes out on cooling which has the formula

$$Na_2B_4O_7 + 10H_2O.$$

This is called *borax* and is regarded as a salt of *tetraboric acid*. This acid is worth looking at for a minute, for it illustrates another of the curious tricks of the hydroxides, both metallic and non-metallic. We have already seen how ready the non-metallic hydroxides are to split off water and form substances intermediate between the hydroxides and oxides. (Refer back to sulphuric acid and nitric acid.) The metallic hydroxides, especially those containing more than two hydroxyl groups, show the same tendency. There are two ways in which this splitting out takes place. Sometimes it consists simply in the splitting out of one or two molecules of water from one molecule of the substance. As an example of a metallic hydroxide which acts in this way, take iron. When ferric hydroxide is boiled with water for some time it becomes denser and less easily dissolved by acids. Analysis has shown that water is split out in this process, and that one of the resulting compounds has the formula FeO(OH). Here the change which has taken place may be represented thus:



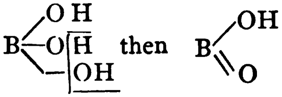
On the other hand, another compound formed under slightly different conditions has the formula $Fe_2O(OH)_4$, and here a different kind of splitting out appears to have taken place. *One molecule of water has split off from two molecules of the hydroxide, one molecule furnishing the hydroxyl, the other the hydrogen*; thus,



The hydroxides of most metals, especially the weakly basic ones, show the same tendencies.

Boron shows both kinds of behavior, and as a result we have at least three *boric acids*, for in the case of non-metals these intermediate compounds are acids.

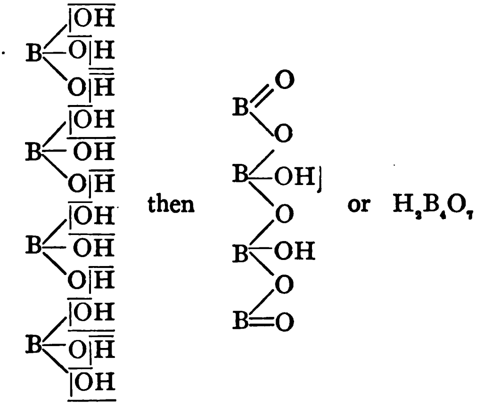
When solid boric acid is carefully heated to 100° the simplest form of water separation takes place. One molecule splits off giving an acid called *metaboric acid.*



or HBO_2

This acid is exactly analogous to nitrous acid (HNO_2). In the case of nitrogen the plain hydroxide is not obtained at all; water splits off immediately, forming nitrous acid. This metaboric acid is easily soluble in water, and gives much more stable salts than those yielded by plain boric acid.

When, however, boric acid is heated to 140° for some time, a different kind of splitting out takes place. *Five molecules of water split off from four molecules of the acid;* perhaps thus:



Three of these water molecules split off by the combined action of two molecules of the acid, two of them take their hydrogen and hydroxyl from the same molecule. This case looks complicated, but it is not particularly so. The acid produced is called *tetraboric acid* and we have already seen that *borax* is its sodium salt.

When the salts of tetraboric acid are treated with strong acids *boric acid* is obtained.

When a water solution of boric acid is boiled *the acid slowly passes off in the steam.* In Tuscany, steam issues from the ground in certain localities, and this steam contains boric acid. By passing the steam into water the boric acid is condensed and crystallizes out when the water is slowly evaporated. In California there is a lake whose waters contain between four and five grams of borax per litre, and large quantities of borax are obtained from this source. Heated in the flame of the Bunsen lamp, borax loses its crystal water and swells up to a white bulky mass which finally melts down to a clear transparent glass. This glass has the power of dissolving metallic oxides, forming double borates; that is, salt of boric acid in which the hydrogen of the acid is replaced partly by sodium, and partly by the other metal. These compounds are often colored. We test for certain metals by making a small clear bead of borax in a loop of platinum wire, touching this bead to a minute fragment of the substance to be tested and heating again in the flame to melt the whole together. The colors given by different metals are given below:

Cobalt	Dark blue.
Manganese	Amethyst color if heated in the outer portions of the flame, colorless in the interior of the flame.
Chromium	Bright green.
Copper	Green when hot, faint blue when cold.

On account of this power of dissolving metallic oxides borax is used for cleaning the surfaces of metals in soldering, brazing and welding.

Boric chloride, BCl_3, can be made by treating boron with chlorine. It is decomposed by water as phosphorus trichloride is.

$$BCl_3 + 3H_2O = B(OH)_3 + 3HCl.$$

Although boron is in most ways allied to the non-metals, it still shows faint traces of metallic behavior. For example, it forms a phosphate BPO_4, which is very stable.

The element itself is obtained by heating boric oxide with potassium.

LABORATORY WORK.

BORON COMPOUNDS.

1. Try the borax bead-tests given above.

2. Prepare some boric acid by dissolving borax in four times its weight of water and adding one third its weight of concentrated sulphuric acid. Cool the solution. Collect and dry the crystals as usual.

3. Since boric acid is not volatile at high temperatures, it decomposes sulphates and drives off sulphuric acid. Mix 0.5 of a gram of *dry* sodic sulphate with about 1.2 grams of boric acid crystals. Heat the mixture as hot as possible in your porcelain crucible (*under the hood or in the open air*). What comes off? Continue the heating till there is no further effect. Cool. Dissolve some of the residue and test for the presence of a sulphate.

Test for the Presence of Boric Acid.—If a piece of yellow turmeric paper be dipped into a slightly acidified solution containing a borate, the paper, when dried, will be reddish brown. Try the test, using borax as the salt to be tested.

ALUMINUM AND ITS COMPOUNDS.

Try the action of the dilute acids upon metallic aluminum. Try also the action of sodic hydroxide. What is given off in this latter case?* Find what volume of hydrogen is yielded by the solution of one gram of aluminum in hydrochloric acid. Calculate the weight of the hydrogen collected. On the simplest possible supposition what value would this give for the atomic weight of aluminum? The specific heat of aluminum is 0.2143. How does this modify your result? What then appears to be the valence of aluminum?

Dissolve a small piece of the metal in hydrochloric acid. Evaporate to hard dryness. Is the residue aluminum chloride? Do you recall any similar case? Can you explain what has happened?

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* Do you recall any other similar case? What was formed in solution in that case? Can you make any suggestion as to what may happen here?

Dissolve another piece in hydrochloric acid. Add slowly, drop by drop, sodic hydroxide as long as precipitate appears. Then add excess of the alkali. What happens?

Aluminum sulphate does not crystallize well, but it forms beautifully crystallized *double salts* with the sulphates of metals having a valence of one. We will prepare one of these which is called *alum*, and which is used for a variety of purposes.

Dissolve one gram of aluminum in hydrochloric acid: add a little more strong sulphuric acid than is needed to convert all the chloride into sulphate (strong sulphuric acid contains about 92% H_2SO_4). Evaporate the solution until the fumes of sulphuric acid *just begin* coming off. Cool thoroughly and carefully; add water. How much aluminic sulphate have you in solution? Weigh out just enough potassic sulphate so to give one molecule of K_2SO_4 for every molecule of $Al_2(SO_4)_3$. Dissolve in water and mix the solutions. Filter if necessary, and evaporate off about one third of the water; then allow the solution to stand. Note carefully the shape of the crystals that separate.

Add sodic carbonate to a solution of aluminic chloride. Wash the precipitate thoroughly and test it. Is it a carbonate?

Dissolve a little aluminum in sodic hydroxide, taking care to have a quantity of aluminum larger than the solution will dissolve even upon boiling. Filter. Pass carbonic dioxide through the solution for some time. Find out what is in solution, and see if you can identify the precipitate also.

LECTURE 53.

ALUMINUM.

THIS metal is white with a fine lustre. Its specific gravity is from 2.5 to 2.7. It is thus about one third as heavy as iron, and one fourth as heavy as silver. Its melting point is about 700°.

It was formerly obtained by heating aluminic chloride with metallic sodium. At present the best metal is obtained by dissolving oxide of aluminum in molten *cryolite*, a double fluoride* of aluminum and sodium (Na_3AlF_6 or $3NaF.AlF_3$) which occurs in Greenland and is imported in large quantities.

Through this "solution" is passed a powerful electric current, when aluminum separates at the negative electrode. The cryolite seems to act toward the aluminum oxide as water does toward salts, acids, and bases, not only dissolving it but in some way or other dissociating it into ions, one of which appears to be aluminum.

The metal forms a white oxide, and when exposed to moist air becomes coated with a thin film of this, which protects it from further action, the film of oxide being very compact and not attacked by water.

Aluminum is already used considerably in making the parts of physical instruments, and in making opera-glasses, telescopes, surveyors' instruments, etc., where lightness is desirable. It is also used somewhat for kitchen utensils. It tarnishes when handled, and has to be frequently cleaned and polished. It has developed little value as a structural material so far, as it is lacking in rigidity. It alloys with most metals. The copper alloys are promising. They are called the *aluminum bronzes*, and they contain about 10% aluminum, have a gold-yellow color, and are not easily tarnished; they are, moreover, very strong.

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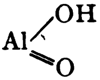
* The fluorides are the salts of hydrofluoric acid HF.

COMPOUNDS OF ALUMINUM.

The compounds of aluminum are very abundant, but their abundance does not make metallic aluminum cheap, for it is at best a difficult matter to extract the metal from its compounds.

All *clays* are mainly silicates of aluminum. *Kaolin* is the purest and whitest form. They have been formed in nature by the slow decomposition of other minerals, such as *feldspar*, which is a silicate of aluminum and potassium. *Mica* is another such double silicate. *Bauxite* is aluminum hydroxide combined with ferric hydroxide. It is used in the preparation of aluminic oxide for the manufacture of metallic aluminum by the electric process described above.

Aluminic oxide, Al_2O_3, occurs in the crystalline form as *ruby* and *sapphire*. The red color of the ruby is caused by the presence of a trace of oxide of chromium; the blue of the sapphire is due to cobaltous oxide. Another naturally occurring form of aluminic oxide is *corundum*, which is used in the form of powder in grinding glass. It can be made artificially from bauxite, or by heating aluminic hydroxide to a very high temperature. It is, when pure, white and difficultly soluble in the acids.

Aluminic hydroxide, $Al(OH)_3$, can be easily prepared by precipitating a solution of any aluminum salt with ammonic hydroxide. (Why cannot sodic hydroxide be used conveniently?) It is a white gelatinous precipitate which clogs the filter-paper badly, and which acts toward alkalies as a weak acid, forming salts, just as if it were an acid of the formula H_3AlO_3. When it is added to a solution of sodic hydroxide it dissolves, and there is formed a salt having the formula Na_3AlO_3 or $AlNa_3O_3$, which is called sodic aluminate. Notice that these salts are analogous to the salts of boric acid (H_3BO_3). It is curious to note, too, that there are some aluminates known which appear to be salts of an acid,  $Al\begin{smallmatrix}\diagup OH\\ \diagdown\!\!\diagdown O\end{smallmatrix}$ or $HAlO_2$, which is aluminic hydroxide minus a molecule of water. These salts are perfectly analogous to the metaborates and nitrites.

Aluminum is a poor salt-former. Its salts with the strong acids react acid toward litmus in water solution, and are broken up more or less completely on evaporating their solutions to dryness; but even such weak and ill-defined salts have their uses, and the salts of aluminum will serve as good examples. In the dyeing of cloth the problem is to fix the dye-stuff on the fibre so firmly that it will not be affected by water or soap. Cloth fibre is sometimes of animal origin, as in wool or silk, and sometimes of vegetable origin, as in cotton. When dyes come in contact with animal fibres the color fixes itself firmly at once, as if the color united in some way with the substance of the fibre forming an insoluble compound. The case is entirely different with cotton or any vegetable fibre. The color does not stick; but if cotton cloth be soaked in a solution of an aluminum salt, and then thoroughly dried, every fibre is not simply covered, but *filled* with a very basic salt, so basic that we can regard it as practically aluminic hydroxide; and if the cloth thus prepared be dipped in the dye, the color apparently unites with the aluminic hydroxide, forming an insoluble compound just as in case of the animal fibres. The salts of aluminum most used for this purpose are the acetate, ($Al(C_2H_3O_2)_3$), and the sulphate, $Al_2(SO_4)_3$, besides *alum*. The salts of other metals, such as iron, zinc, and tin, are used in the same way. They are called *mordants*, since their office is to make the color "bite in" and hold its place.

It will easily be seen that if the mordant be put on only in spots the color will only stick where the mordant is. This enables us to print patterns on cotton cloth, by printing the pattern on to the cloth in the mordant, dipping the cloth in the dye, and then washing it out, when the pattern comes out in the required color. Sometimes the mordant and the color are mixed and made into a paste with gum-arabic or wheat flour. The mixture is then used just as printer's ink is in ordinary printing to print the pattern on the cloth. This is called "topical printing."

Alum is a double sulphate of aluminum and potassium. It is made by roasting certain rather easily disintegrated rocks containing aluminum silicate and then treating them with sulphuric acid. To the solution thus obtained is added potassic sulphate, and the alum is crystallized out. It forms beautiful octahedral crystals.

The formula is sometimes written $Al_2K_2(SO_4)_4 + 24H_2O$, and sometimes $AlK(SO_4)_2 + 12H_2O$. There is at present no way of deciding between the two. The simpler formula is as well in accord with the facts at present known as the more complicated one.

LECTURE 53.

ALUMINUM, CONCLUDED.

Earthenware and Porcelain.—In making earthenware, common clay, sand, and feldspar are mixed with water till the mixture has about the consistency of dough; the mixture is very plastic, and can be easily moulded into any desired shape. The articles when moulded are carefully dried and heated in special furnaces, at a red heat. This gives a porous earthenware which has to be "glazed" to make it water-tight. Porcelain is made in much the same way, only in this case the purest obtainable clay (kaolin) and pure white feldspar are used, and mixed in such proportions that the mixture on "firing" or heating to a high temperature fuses together into a white semi-translucent mass.*

Glazing is accomplished in one of two ways. In case of porcelain the articles are dipped into water in which is suspended sand and feldspar in exceedingly fine powder, and in such proportions as to be more fusible than the ware itself. After dipping, the articles are dried and then fired at a high temperature, in order to melt the glaze uniformly over the surface. Another method that is sometimes employed in case of earthenware is to dip the article into water in which finely powdered *litharge* (an oxide of lead) is suspended. On firing, lead silicate is formed, and this melts and forms the glaze.*

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* The distinction, then, between earthenware or pottery and porcelain is that earthenware is porous, and has only been "fired" at a red heat, while porcelain is semi-fused and translucent, having been fired at a very high temperature. In some cases the only sure method of telling is to apply the tongue to a broken surface of the dish when it will adhere if the material is earthenware.

In some of the rougher forms of stoneware, common salt is thrown into the furnace toward the end of the firing. This volatilizes, and the hot objects, which contain iron in the form of silicate, react with this, forming sodic silicate, which fuses to a glaze, and ferric chloride, which volatilizes.

Common bricks are made from ordinary impure clay, which usually contains more or less iron in the form of ferrous carbonate and silicate. The bricks after being formed are built up into piles and fired at a comparatively low temperature. The red color is due to the oxidation of the iron from a ferrous to a ferric compound, the final product being ferric oxide.

Ultramarine is a very beautiful blue substance which is used extensively as a paint. It is found in nature as *lapis lazuli*, in comparatively small quantities, and was formerly very expensive. Now it is very cheap, for methods have been found by which it can be very easily made on the large scale. It is a silicate of aluminum and sodium containing sulphur, and is made artificially by melting together sodic carbonate, clay, and sulphur. By varying the proportions and the method of heating a number of different colored products can be obtained besides the blue.

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* If colored figures or patterns are to be put on the articles, they can either be painted on the unglazed ware before it is dipped and fired, or they can be put on the glaze and "burnt in." In the first case the colors are usually metallic oxides or other compounds which will stand a high temperature, and which will melt into the glaze, forming colored glasses. In the second case the colors used are practically nothing but colored glasses ground very fine.

LECTURE 54.

IRON—COBALT—NICKEL.

THESE metals constitute a curious group, in that their atomic weights are very close together. This is a different kind of relationship from any we have encountered thus far, and is a representative of a peculiar kind of *triad* noticed and mentioned by Döbereiner. There are at least two other such *triads*.

The elements we are now considering have many remarkable points of resemblance. They decompose water at a dull-red heat, forming oxides and liberating hydrogen. Each forms two sets of salts and other compounds. In one of these series the valence of the metal appears to be *two;* in the other, *three.*

They are all white, moderately heavy metals, with high melting-points, fairly permanent in dry air, and are very lustrous when polished.

Metallic iron has not been found occurring in nature until recently. Some varieties of meteorites consist mainly of metallic iron with small quantities of cobalt and nickel. Meteoric dust is constantly falling on the earth's surface, and this dust contains more or less iron. Quite recently there has been found and described what seems to be a genuine specimen of terrestrial iron. Neither cobalt nor nickel occurs in nature in the free condition.

The compounds of iron are very abundant and almost universally distributed. The principal iron ores are one of its oxides and one of its carbonates. These are found in immense deposits in various parts of this country, England, and Europe. Iron compounds are present in almost all rocks, and when these rocks "weather" or decompose and fall to pieces, as they do under the long-continued action of wind, rain, and frost, the iron compounds pass into the soil. Most natural waters carry traces of iron compounds dissolved out from the soil. The green coloring-matter of leaves contain iron, and so does the blood of animals.

LABORATORY WORK.

Try the action of dilute hydrochloric, nitric, and sulphuric acids upon iron.*

The fact that there are two series of iron-salts has been mentioned. Those in which the valence of iron is two are called the *ferrous* compounds; those in which it is three are called the *ferric* compounds. We will now proceed to some work which will bring out the relations between the two series:

1. Prepare a solution of *ferrous sulphate.* This can be done by dissolving iron in dilute sulphuric acid, taking care to exclude air, and to have rather more iron present than the acid will dissolve.

The best way of proceeding is to place the iron (about 2 grams) in a 100 c.c. flask with about 30 c.c. dilute sulphuric acid; attach a delivery-tube dipping under water and warm the contents of of the flask. When there is no further action on removing the lamp enough iron will have dissolved. Half of this solution is now to be set aside. We shall presently use it to make a solution of ferric sulphate by which to study the ferric compounds. The other half is to be used in preparing some of the ferrous salts and other compounds.

Ferrous Chloride.—Of course it is not practicable to convert ferrous sulphate *directly* into ferrous chloride—that is, by acting upon it with hydrochloric acid. (Why is it not practicable?) How, then, can we manage to convert a portion of our ferrous sulphate *completely* into chloride? Think out a method by which this can be done; and while you are about it, think out a method by which you can convert another portion into ferrous nitrate, which is a similar case.

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* Use clippings of fine iron wire or "card-teeth" if available. Cuttings of thin sheet-iron will do.

When you have obtained solutions of the two desired salts the next thing to do is to see if they crystallize well. It is not best to boil them down in contact with the air. It will be better to place one in a 50 c.c. flask whose mouth is loosely stopped by a little bulb blown on the end of a piece of small tubing, and the other in your evaporating-dish, an inverted funnel being set down into the dish to serve as a loose cover. Either of these arrangements admits of a solution being concentrated practically out of contact with the air, since in both cases the space above the solution is kept full of steam. When the solutions have been concentrated to about one third their original bulk set them aside and see if crystals separate on standing. If any do, first describe and make drawings of them,* using a lens if necessary to get at the form.† Next dry a few crystals of each salt by pressing with filter-paper, and dissolve them in a few drops of water in separate watch-glasses. Try the action of the solution upon red and blue litmus-paper. Boil the solutions. Does any change take place? Cool and try the litmus tests again. Powder a little of each salt and place the powders upon bits of filter-paper. Allow them to stand exposed to the air for some time, noting changes if any take place.

You can also concentrate a little of your original ferrous sulphate solution, and make the same experiments upon the crystals. Do any of these salts contain crystal-water? How can you decide this point? Plan a method and see what results it yields.

Ferrous Carbonate.—How will you prepare this salt? Carry out the method and note carefully the color of the compound at the instant of its appearance. What changes does it undergo (in appearance)?

The following method will enable you to get a better idea of the looks of the original substance.

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* See foot-note to p. 286.

† A very fair lens can be extemporized by filling the double convex space between two watch-glasses with distilled-water. The watch-glasses can be stuck together with label-paper.

Dissolve a crystal of ferrous sulphate in half a test-tubeful of water. Add solid *primary sodic carbonate* ($HNaCO_3$). Rapidly filter off the precipitate and spread it out on the filter-paper, noting changes from time to time.

Ferrous Hydroxide.—How prepared? Spread some out on the filter-paper and carefully note from time to time the color changes.

We will now pass to the ferric compounds.

Take the ferrous sulphate solution which was set aside for making a ferric solution. Warm it and add to it drop by drop a solution of hydrogen dioxide (H_2O_2).* This substance is a most rapid and powerful *oxidizing agent*, decomposing slowly into oxygen and water even when left to itself, and very rapidly in contact with any substance upon which oxygen acts. Solutions containing salts in which the metal is at one of its lowest valences are acted upon by oxygen, especially oxygen liberated directly in the solution, the result being the formation of the corresponding salt in which the metal has a higher valence. Note the effect upon the solution as the hydrogen dioxide is dropped in. Continue the addition till no further change is noticed. You now have a solution of *ferric sulphate*.† The same result can be reached by adding to the acid solution of ferrous sulphate a few drops of strong nitric acid, and boiling; in fact there are a number of substances which act as oxidizing agents, but they are substances we have studied. Try to crystallize out some of the ferric sulphate just as in case of the ferrous salt. In what respects does it differ from the ferrous salt? What is its action upon litmus?

Ferric Chloride.—Boil a little iron with concentrated hydrochloric acid. Add hydrogen dioxide. Evaporate some of the solution. Can you obtain crystals? Does the residue redissolve to a clear solution? Does this substance seem to be much like ferrous chloride?

Ferric Hydroxide.—Prepare some and compare it with the ferrous compound.

Attempt to prepare ferric carbonate. Filter it off, and wash carefully and thoroughly six or seven times with water. Try a little with dilute hydrochloric acid. Does it effervesce? Is it a carbonate? Which of the iron compounds you have seen thus far does it most resemble? What differences do you see, so far, between the ferrous and ferric compounds as regards looks and behavior? Sum them up fully in your notes. Which are the most permanent under ordinary circumstances? What do *present appearances* seem to suggest as a possible explanation of the changes in the ferrous compounds when they are exposed to the air? We could investigate this point better if we had a way of distinguishing sharply between the ferrous and ferric compounds; and here is the method:

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* This can be obtained at any drugstore, or can be made by dropping barium dioxide into dilute sulphuric acid.

† The reaction will be taken up again farther on.

Ferrous solutions give a deep dark-blue precipitate when *potassic ferricyanide* solution is added.

Ferric solutions give a precipitate of exactly the same color when *potassic ferrocyanide* solution is added. *Pay no attention to any other result.* If an iron solution gives a very dark blue precipitate with potassic ferrocyanide it contains a ferric salt. If it gives a precipitate of any other color, disregard it. The same applies to the test for ferrous compounds.

Of course if a solution answers to both reagents it contains a mixture of ferrous and ferric salts.

Conversion of Ferric into Ferrous Salts.—We have seen how by the use of substances which readily give up oxygen (oxidizing agents) we can in general pass from the salt in which the metal has its lower valence to that in which it has its higher valence.

The reverse step can be taken by using strong *deoxidizing agents*—substances which, in solution, unite readily with oxygen. One of the best is *nascent hydrogen*, that is, hydrogen *liberated in the solution*, which owes, as we have seen, its power to the fact that the hydrogen is in the atomic state. The hydrogen may be generated by adding to the solution some acid and metallic iron or zinc and allowing the action to go on until the test shows the reduction to be complete. Try reducing a solution of ferric sulphate in this way, using about 5 c.c. of a rather dilute solution.

Hydrogen sulphide acts as a powerful deoxidizer or *reducing agent* because of the ease with which it decomposes into hydrogen and sulphur whenever there is anything in the field with which hydrogen unites readily under the circumstances. Bubble some hydrogen sulphide through ferric sulphate solution until a drop taken out and tested as above shows the reduction to be complete. What separates from the solution? What does it look like? See if you can find out what it is.

Sulphurous acid and the sulphites are good reducers, since they so readily take up oxygen and become sulphuric acid or sulphates. Add a little sodic sulphite to a slightly acid solution of ferric sulphate. Test as before.

All forms of animal or vegetable matter act as reducing agents, and it is not surprising that when iron salts are formed under the surface of the soil in contact with water the salts are almost invariably ferrous. On the other hand, the naturally occurring iron compounds that exist in contact with the air are always ferric.

LECTURE 55.

IRON, COBALT, AND NICKEL, CONTINUED.

THE first point to consider is the ores of iron and the manner in which they have been deposited. The simplest one to consider first is ferrous carbonate, or *siderite*. It is a whitish-gray mineral which is found in large deposits in this country and in England and Scotland. It is frequently met with in close contact with coal-beds. It has been deposited by a process much the same as that which has deposited limestone. Ferrous carbonate dissolves in water containing carbonic dioxide, just as calcic carbonate does, and it probably exists in solution as an acid ferrous carbonate, $H_2Fe(CO_3)_2$, analogous to $H_2Ca(CO_3)_2$. This fact enables us to understand how it is that ferrous oxide is dissolved by water containing carbonic dioxide. The oxide is first changed into ferrous carbonate, then to the acid ferrous carbonate, which is soluble in water. The water sinks into the ground with its charge of dissolved iron compounds and flows away. Its subsequent history is determined entirely by its surroundings. It may finally settle into some basin-shaped depression, out of contact with the air, where it will slowly deposit its ferrous carbonate as such, and this will the more surely be the result if deoxidizing substances (like decaying vegetable matter, or any form, in fact, of organic matter) be present. It is probably for this reason that most of the iron of the coal measures is ferrous carbonate. Again, the solution may finally collect in some hollow or basin on the surface of the earth and in contact with the air, and what takes place under these circumstances can be easily understood if one recalls how the stagnant water that collects in ditches or clay-pits behaves on standing. This water practically always contains dissolved ferrous carbonate, and such water, on standing exposed to the air, becomes covered with a thin film which shows a play of colors in sunlight like an oil film, for which it is often mistaken. This film consists essentially of ferric oxide, or rather a mixture of oxide and hydroxide, resulting from the oxidation of ferrous carbonate to ferric carbonate, which, as we have seen in the laboratory, at once loses CO_2 and forms ferric hydroxide. It subsequently sinks to the bottom, where it accumulates as a reddish-brown mud. By this process in the course of countless ages, beds of iron ore are accumulated. It will perhaps be worth while to see how these facts can be approximately represented in the form of reactions.

First, however, we must take account of a fact we have not as yet noticed, namely that a very large part of the iron oxide encountered by the water in its course over rocks and through the soil is in the shape of *ferric oxide*, which is not dissolved by water containing carbonic dioxide. Here comes in the important fact that the dissolved organic matter carried by most surface waters acts upon the ferric oxide and reduces it to ferrous oxide, which is then in a position to be dissolved by the water, as has been described. This reduction by organic matter we will not attempt to represent in form of a reaction.

The action of water and carbonic dioxide upon ferrous oxide is perhaps

$$FeO + 2CO_2 + H_2O = H_2Fe(CO_3)_2.$$

When the solution comes out in contact with the air,

$$2FeCO_3 + 3H_2O + O = 2Fe(OH)_3 + 2CO_2.$$

These reactions can mean quite a little to us, for we have seen in the laboratory a set of changes take place which are practically the same as those represented by these reactions, and it is possible to imitate almost exactly what takes place if time is available.

Moreover the reduction of ferric to ferrous oxide by organic matter is a very familiar and common sight. Whenever a nail is driven into a board and allowed to stand exposed to the weather for some time, a greenish-black spot gradually spreads out from the nail into the wood, and the wood is finally found to be soft and "punky" all round the place where the nail was driven. Old boards on fences are always rotted away round the nails. Moreover, when cloth becomes stained with iron-rust it always weakens and rots where the spots of iron-rust are. Both these are cases of the reducing action of organic matter upon ferric oxide. Oxygen is given up to the wood or cloth by the ferric oxide.

The following easily-tried experiment will, perhaps, serve to fix in mind what has been said :

Saturate a *very dilute* solution of ferrous sulphate with carbonic dioxide. Add about two drops of a strong solution of sodic bicarbonate (primary sodic carbonate). This should be sufficient (if the iron solution is dilute enough) to convert all the ferrous sulphate into ferrous carbonate. Bubble carbonic dioxide through the solution for some minutes. Then filter rapidly into an evaporating dish, which is now to be set aside where it can remain undisturbed. In a few hours the film can be seen on the surface of the solution, and in the course of time it will, partially at least, break from the surface and sink to the bottom.

It will not be best to try to go into details as to the ores of nickel and cobalt, but the remark may be made once for all that the accumulation of metals and other substances not metals as well, either in the fissures of rocks as "veins," distributed through rocks in the form of nuggets, or in extensive deposits or "beds," has been brought about mostly through the agency of water, organic matter, and carbonic dioxide.

Among these three agencies by far the most important and universal is water, and the conditions which make the surface of the earth fit for sustaining the many and various existing forms of animal and vegetable life are almost wholly due to its action in one form or another.

Extraction of Iron from its Ores.—The process of extracting iron is, in principle, very simple. The ores are first treated in such a way as to bring them to the state of oxide of iron; and the oxide thus produced is reduced to metal by heating to a high temperature with carbon (coke, coal, or charcoal).

If the ore is a good red hæmatite containing very little water, it needs no preliminary treatment. The brown hæmatites, which are mixtures of oxide and hydroxide, require heating in the air, or *roasting* as it is called. This decomposes the hydroxide and leaves the oxide. Ferrous carbonate requires roasting so as to drive off water which it often contains as a mechanically held impurity, and also to decompose the carbonate with evolution of carbonic dioxide, leaving ferrous oxide, which is at once oxidized by the oxygen of the air to ferric oxide; thus,

$$2FeO + O = Fe_2O_3.$$

The ores thus treated are ready for reduction. With small furnaces and moderately high temperatures we obtain a spongy, malleable, pasty *bloom* or lump of reduced iron, which melts only at a very high temperature and then is not very fluid: such iron is, however, very easily rolled and hammered at a red heat. This was the earliest form in which iron was obtained, and the manufacture is still carried on with furnaces of varying dimensions and shapes in India, some parts of Spain, Norway, and Sweden, and in some parts of the United States and Canada. The fuel is usually charcoal, so the furnaces have to be located where charcoal is cheap. The iron produced by this process is called *wrought iron*, and is still extensively used, though not nearly so much as formerly. It is not pure iron, though it is the nearest to it of any of the forms of commercial iron.

The great starting-point in all kinds of iron manufacture to-day is the manufacture of *cast iron*, which is not only a very useful substance in itself, but is the raw material in the manufacture of the different forms of structural iron and steel.

To make cast iron the ore is reduced in huge *blast-furnaces*, which are from 30 to 100 feet high and from 10 to 20 feet in diameter at the widest part. The inside lines of such a furnace are not unlike those of a common lamp-chimney, the only marked difference being that the furnace is narrower in proportion to its height. These furnaces are run by forced draught, air being blown in under a pressure of from 8 to 15 pounds per square inch through blast-nozzles, or *tuyères* as they are called, of which there are commonly seven, and which enter through the walls of the furnace a few feet above the hearth.

The top of the furnace is closed, but there is an arrangement by which it can be momentarily opened for the introduction of more material. The waste gases from the top of the furnace are carried off by a large pipe and used (1) for heating the air which is to be blown into the furnace through the tuyères; (2) as fuel under the numerous steam-boilers required round such an establishment.

The materials charged into the furnace are (1) the suitably prepared ore, in lumps averaging about the size of a large croquet-ball; (2) fuel (usually coke or anthracite coal); (3) limestone—for this reason: the ore always contains some impurities and the coal always leaves some ash. Since the furnace is to run continuously night and day for months, perhaps for years, it follows that these impurities will after a while collect in the furnace to considerable amounts, and what is worse, they are generally hard to melt, being largely silicon dioxide, which is chemically the same as white sand. The limestone is added because the silicon dioxide (SiO_2) is an acid-forming oxide, and consequently reacts with the calcic carbonate, forming calcic silicate ($CaSiO_3$), which melts with comparative ease. The final fate of this mixture of fuel, ore, and limestone in its slow descent through the furnace, where it is constantly exposed to higher and higher temperatures as it descends, is this: (1) The oxide of iron is reduced to metal. This reduction is effected mainly by carbon monoxide (CO), which in turn results from the action of the hot coal upon carbonic dioxide formed by the burning of coal farther down in the furnace. The reactions involved in these processes and in the reduction of the ferric oxide may be simply represented thus:

1. $C + O_2 = CO_2$.
2. $CO_2 + C = 2CO$.
3. $Fe_2O_3 + 3CO = Fe_2 + 3CO_2$.

(2) *The reduced metal combines with carbon*, the amount taken up varying with the temperature and with the nature of the charge. The alloy of iron and carbon thus produced is fusible, and trickles down through the white-hot fuel, collecting finally in a fluid layer at the bottom of the furnace, whence it is drawn off about once in twelve hours through a hole provided for the purpose, which is kept stopped with clay except at the "casting time." (3) The limestone meanwhile licks up the silica of the coal-ash and ore and converts it into the easily fusible calcic silicate, which is technically called *slag*:

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2.$$

This slag (which is really much more complicated in composition than the above formula would indicate) trickles down over the charge, and finally reaches the bottom or ***hearth*** of the furnace, where it collects on top of the iron as a fluid layer, which is drawn off by a separate tapping-hole, called the *cinder-notch*, "cinder" being the furnaceman's term for slag. If all goes well, then the programme is simply to charge, at intervals, fuel, ore, and limestone into the top of the furnace, and draw off the iron and slag at the regular times. In many cases all does go well, and the furnace remains "in blast" for two or three years at least, without once ceasing its steady output of cast iron.

When the iron is drawn off it runs into a gridiron-shaped set of moulds made in a sand bed, so that the iron is cast into bars about two feet long and five inches or so deep, whose cross-section is shaped as shown in Fig. 49. These bars are called "pigs," and cast iron is frequently called "pig iron."

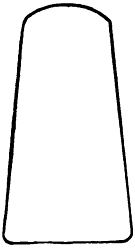


FIG. 49.

When the iron cools, some of the carbon crystallizes out in form of gray, glittering crystals of *graphite*, which are left undissolved when the iron is treated with hydrochloric acid. Some of the carbon is left dissolved in the iron, or combined with it. The relative amounts of these two kinds of carbon vary with the temperature of the furnace and the nature of the charge, and pig irons are classified commercially by the looks of the end of the bar when it is broken, the iron being coarse-grained and dull-looking when there is much graphite, and finer grained and whiter as the amount of graphite decreases. The irons richest in graphite form the basis of the iron mixtures used for making castings. The other varieties are used in manufacturing steel. Cast iron contains many other things besides carbon. The principal things are silicon, sulphur, phosphorus, and manganese. These, together with the carbon, amount to from 6% to 8% of the weight of the pig, and each one has a very decided effect upon the properties of the metal, which, as will now be seen, is a rather complex substance.

Steel may be roughly defined as the metal produced by any one of the three following processes:

1. The crucible process.
2. The Bessemer process.
3. The open-hearth process.

In the *crucible process* a carefully made-up mixture of scrap steel and iron, with a little manganese dioxide, is melted down in large clay crucibles and cast into *ingots*, or else poured at once into moulds to make castings.

In the *Bessemer process* cast iron containing about 2% silicon is melted and poured into a huge egg-shaped vessel called a *converter*. This vessel is carefully lined with fire-brick, and has in its bottom a number of fine holes through which air can be blown up through the melted iron. The oxygen of the air seizes upon the silicon and carbon mainly, and burns them. The "blow" is over in from eight to fifteen minutes, depending upon the quantity of metal operated upon, which is usually from five to ten tons.

Next there is added to the contents of the converter enough of an iron rich in carbon and manganese (called *spiegeleisen*, or, more commonly, *spiegel*) to give the desired percentage of carbon and manganese. The steel made by this process is used almost entirely for rails, and contains about 0.35% carbon as an average.

In the *open-hearth process* a mixture of pig iron and scrap steel or iron is melted down on the saucer-shaped floor or hearth of an oblong furnace having a low roof and charging-doors at the side, and which is fed by a mixture of coal-gas and air so arranged that the effect is practically that of an enormous Bunsen flame. When it is melted down the metal is usually treated with oxide of iron in the form of iron ore. The result of this treatment is that the oxide is reduced to metal by the carbon which the molten metal contains, the carbon uniting with the oxygen and going off as gaseous carbon monoxide. When the percentage of carbon has been brought down to a certain point (which is ascertained by ladling out a sample of the metal, pouring it into a mould, breaking the bar and examining the fracture), spiegel or *ferromanganese* (another alloy of iron with about 80% manganese, spiegel containing only about 12%) is added, together with pig iron and *ferrosilicon* (an alloy of iron and silicon), the amounts being determined by the quality of steel wanted. The whole charge is then "tapped off." This steel is used in building bridges and roofs and almost all kinds of machinery. It is also extensively used in making large guns, ship-plate, and boiler-plate. It is strong and elastic, and is often free from any sign of brittleness, so that a rod made of it can be tied into a knot or bent double on itself cold without showing any sign of a crack.

When steel contains more than about 0.5% carbon it begins to acquire the property of *hardening* when heated to a cherry-red and plunged into water or oil. Such steel is used in making chisels, axes, and all other forms of cutting tools. If a piece of steel which has been hardened be heated up again *below redness* slowly and carefully, it gradually becomes soft again, and the same thing happens if it be heated up to a cherry-red heat and allowed to cool slowly. This is called *annealing*. Finally, if a piece of steel be hardened, then heated up gently, a film will appear on the surface of the metal, which is at first straw-color, and then passes through gradually darkening yellows and browns until it is dark blue and finally black. If as soon as the straw-color appears, the steel be plunged into water, it will retain just the degree of hardness it had at the moment of quenching. This process is called *tempering*, and the tint at which it is quenched determines the hardness and toughness of the metal. Speaking generally, the yellow tints correspond to very hard, brittle metal, and are used for cutting tools with very keen edges, like razors, while the dark brown and blue tempers are not so hard, but tougher, and are used in tempering springs. Steel contains roughly from 0.1% to 1.75% carbon, most of which is combined. It always contains manganese, besides silicon, sulphur, and phosphorus in very small quantities. Each of these has its effect, and requires careful regulation.

Cobalt and nickel are reduced from their oxides in the same way as iron is, but their ores are more difficult to handle, being largely *arsenides* of cobalt or nickel. These ores are roasted to drive off the arsenic and leave the oxide of the metal, which is then reduced with coal or charcoal. The metals are much like iron in appearance. Cobalt has no commercial uses. Nickel is at present used in plating and in making "nickel steel,"' an alloy of iron with a few per cent of nickel, which is used in making armor-plate. Nickel is also a constituent of the one-cent and five-cent coins. The five-cent piece contains 25% nickel and 75% copper.

COMPOUNDS OF IRON.

In general, as our studies in the laboratory have shown, the ferrous compounds are more definite and crystallize better than the ferric compounds. Only two of them need be mentioned: *ferrous sulphide* (FeS), which is made by melting together iron and sulphur in the proportion of their atomic weights, and which is used for making hydrogen sulphide in the laboratory, and *ferrous sulphate*, which is sometimes found in crystals in the crevices of rocks, where it has been formed by the oxidation of *pyrite*, which is a sulphide of iron having the formula FeS_2, found in coal and in rocks in form of brass-yellow crystals, and occasionally mistaken for gold.

It is obtained as a by-product in wire works where the scale is taken off the wire by dilute sulphuric acid. The waste acid liquors are evaporated and the ferrous sulphate crystallized out. It is called "green vitriol," and it carries seven molecules of crystal-water, like zincic sulphate and magnesic sulphate. When ferrous sulphate and sodic, potassic, or ammonic sulphate are mixed in solution in the proportion of their molecular weights, there crystallize out, on concentrating the solution, greenish salts, which have the formulæ

$FeNa_2(SO_4)_2 + 6H_2O$ or $FeSO_4.Na_2SO_4$,
$FeK_2(SO_4)_2 + 6H_2O$ " $FeSO_4.K_2SO_4$,
$Fe(NH_4)_2(SO_4)_2 + 6H_2O$ " $FeSO_4.(NH_4)_2SO_4$,

according to which sulphate was used.

These salts are appropriately called *double salts*. They are beautifully crystalline and more stable and permanent than the original ferrous sulphate. There a great many of these double salts, but we know very little about their constitution. Ferrous sulphate is used in dyeing, and in the manufacture of ink. It acts also as a deodorizer.

None of the ferric compounds are of special importance. As a rule the salts do not crystallize well, but it is interesting to note that while ferric sulphate, for example, does not itself crystallize well, it forms double salts with sodic, potassic, or ammonic sulphate, which crystallize beautifully. This is true in general of double salts in which one of the constituents is a sodium, potassium, or ammonium salt. The ferric salts all react acid in water solution. Their solutions contain very slightly dissociated *basic salts*—that is, salts in which part of the acid ion is replaced by hydroxyl, such as $FeCl(OH)_2$, basic ferric chloride; $Fe(SO_4)(OH)$, basic ferric sulphate, etc. The formation of these basic salts when the salt is dissolved in water, removes some hydroxyl ions from solution, thus leaving an excess of hydrogen ions, hence the acidity. (See under Zincic Chloride, p. 351.)

Cyanides of Iron.—These compounds of iron are mentioned because they bring us in contact with a new kind of double salts.

The *cyanides* are the salts of *hydrocyanic acid*, which has the formula HCN and forms salts like KCN, $Ba(CN)_2$, etc. Since this CN group seems to travel as a whole and behave like an element, it is sometimes written Cy and called the *cyanogen group.*

Neither of the two cyanides of iron, $FeCy_2$ or $FeCy_3$, is important, but their double sodium and potassium salts are very interesting and important.

When ferrous cyanide is added to a solution of potassic cyanide it dissolves, and on evaporating and cooling the solution yellow crystals separate which prove on careful analysis to contain iron, cyanogen, and potassium, and in such proportions as to point to the formula K_4FeCy_6 or $4KCy.FeCy_2$, the substance appearing as a double cyanide of potassium and iron. The curious thing about it is this: most double salts in water solution act simply like a mixture of the salts composing them. For example, we can precipitate ferrous carbonate from a solution of ferrous ammonium sulphate just as easily as from ferrous sulphate. The solution acts simply like a mixture of ammonic sulphate and ferrous sulphate; but this double cyanide of iron and potassium gives in water solution none of the ordinary iron precipitates with reagents. On adding sodic carbonate there is no precipitate, and, in short, we could not use this solution for making the ordinary iron salts, for it acts as if it contained no iron at all. When we add to it solutions containing salts of other metals, however, we get precipitates which prove to contain the metal, iron, and cyanogen. The dissociation theory explains these curious facts thus: instead of splitting down into potassium, iron, and cyanogen ions, the salt splits into two ions, one of which is potassium and the other $FeCy_6$. The solution then contains no iron ions and so gives no iron reactions. The salt then may be regarded as a potassium salt of an acid H_4FeCy_6, and when the solution of the potassium salt is treated with strong hydrochloric acid a white precipitate falls which has the above constitution, potassic chloride remaining in solution. This acid has been named *hydroferrocyanic acid* and the salts are called *ferrocyanides.* We have used the potassium salt as a test for ferric compounds and we are now in a position to understand its action. When this salt is added to a ferric solution we get a *ferric ferrocyanide* precipitated. The reaction looks a little complicated, but it is not at all so:

$$3K_4FeCy_6 + 4FeCl_3 = Fe_4(FeCy_6)_3 + 12KCl.$$

This precipitate is dark blue. The color is very fine, and a compound very similar to the one given above is used as a pigment under the name of *Prussian blue.*

Ferric cyanide, $FeCy_3$, also forms a double salt having the formula K_3FeCy_6, and the same facts come to light on close study of it. It is called potassic ferricyanide, and its use in testing for ferrous compounds is based upon the fact that with ferrous solutions it gives a dark-blue precipitate of *ferrous ferricyanide* (Turnbull's blue), thus:

$$3FeSO_4 + 2K_3FeCy_6 = Fe_3(FeCy_6)_2 + 3K_2SO_4.$$

These double salts are among the most marked instances where the two uniting salts form a *complex ion*, but the action is imitated in a very marked manner by many of the double chlorides, bromides, and iodides, as we shall have constant occasion to see.

COBALT AND NICKEL COMPOUNDS.

The cobaltous and nickelous salts are the most stable. The cobaltic and nickelic salts are difficult to prepare.

The cobaltous salts are generally pink, the nickelous salts green. Cobaltous chloride is used in the so-called invisible inks. The writing is not visible unless the paper be heated, when the crystal water is driven off from the chloride, which darkens in color and makes the writing visible.

Nickelous sulphate, $NiSO_4,7H_2O$, a bright-green salt, forms double salts with the sulphates of sodium, potassium, and ammonium. The ammonium double salt is $Ni(NH_4)_2(SO_4)_2 + 6H_2O$ and is extensively used in nickel-plating. This matter of plating will be taken up again under silver and gold.

LECTURE 56.

MANGANESE AND CHROMIUM.

As will be seen on referring to the Mendeléeff table these two metals are placed in different groups. If we were to stick strictly to the table, we should study chromium with sulphur, selenium, and tellurium; and manganese with chlorine, bromine, iodine, and fluorine. There are, however, good reasons for not following this method. Manganese and chromium are both predominantly metallic, and being in adjacent groups it is not very surprising that they have many points in common. In the aggregate they are much more like one another than they are like the other members of their respective groups. So it will be best to take them together, and to content ourselves with pointing out as we go along the respects in which they show the group characteristics.

The most distinctive point about them is that *they form very stable and important salts analogous to the sulphates, but with manganese or chromium in the place of sulphur.* These salts are called *manganates* and *chromates*. Manganese, moreover, forms salts which show themselves to be derived from an acid, $HMnO_4$, and which are called the *permanganates*. Chromium imitates manganese in a feeble way in this regard, forming a very unstable *perchromic acid*, $HCrO_4$.

We will begin our study with manganese.

It is never found in nature as the pure metal. Its most common compound is *pyrolusite*, a manganese oxide having the formula MnO_2. It is a black, crystalline mineral. From it most of the manganese compounds are made. There are in all six oxides of manganese, named as follows:

MnO, Manganese oxide	A basic oxide forming fairly stable salts with the acids.
Mn_2O_3, Manganic oxide	A weakly basic oxide forming only a few unstable salts.
MnO_2, Manganese dioxide or Manganic peroxide	An oxide which according to circumstances is weakly basic or weakly acidic.
Mn_3O_4, Mangano-manganic oxide	Neither acid nor basic.
(MnO_3) unknown	Salts of the corresponding acid, H_2MnO_4, are known.
Mn_2O_7, Manganese heptoxide or *permanganic anhydride*	A strong acid-forming oxide.

As to the preparation of the manganese compounds the matter may all be summed up thus: Starting with manganic dioxide we can make either the higher or lower compounds according to the method of attack. Treated with the strong acids with or without reducing agents it yields the manganous salts, which correspond closely to the ferrous salts, and in which the valence of manganese is *two*. These salts are of no special importance. They are generally flesh-color or pink, and crystallize fairly well, though the double salts which they form with the corresponding sodium, potassium, and ammonium salts are more stable and crystallize better.

The reaction by which manganous chloride is made from manganese dioxide is of great commercial importance. When manganese dioxide is treated with strong hydrochloric acid in the cold, it slowly dissolves, forming a deep greenish-brown solution, which when heated *gives off chlorine* abundantly, leaving manganous chloride in solution. Careful study of the reaction has led to the conclusion that the brown solution contains a tetrachloride of manganese ($MnCl_4$), corresponding to manganese dioxide (MnO_2), and that this substance on heating decomposes with loss of half its chlorine. The reaction would then be represented as follows:

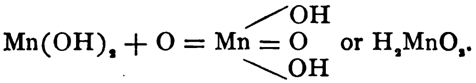
1. $MnO_2 + 4HCl = MnCl_4 + 2H_2O$.
2. $MnCl_4 = MnCl_2 + Cl_2$.

This is a very important reaction, for the chlorine used in bleaching is prepared by this method. Enormous quantities of manganous chloride result, of course, and as pyrolusite is not especially cheap, there have been many attempts to find a method for reconverting the manganous chloride into manganese dioxide, so that it could be used again. The most successful process is that of Weldon. The steps are:

1. The solution of manganous chloride is treated with slaked lime, $Ca(OH)_2$, by which manganous hydroxide is produced:

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2.$$

2. The manganous hydroxide is mixed with more slaked lime in the proportion of one molecule of $Ca(OH)_2$ for every molecule of $Mn(OH)_2$, and a current of steam mixed with air is blown through the mixture. Under these circumstances the first thing that happens is probably the direct addition of oxygen to the $Mn(OH)_2$; the manganese "changing its valence" from two to four perhaps thus:



$$Mn(OH)_2 + O = Mn\begin{smallmatrix}\diagup OH\\ = O\\ \diagdown OH\end{smallmatrix} \text{ or } H_2MnO_3.$$

This substance acts as a weak acid and immediately acts upon the calcic hydroxide, forming the calcium salt:

$$Ca(OH)_2 + H_2MnO_3 = CaMnO_3 + 2H_2O.$$

(*Notice that this acid is analogous in formula to sulphurous acid, just as manganese dioxide is analogous to sulphurous oxide.*) This salt is called by the chemists *calcic manganite*, but its technical name is "manganese mud." When it is treated with strong hydrochloric acid it yields calcic chloride, water, chlorine, and manganous chloride.

The manganic salts are unstable and unimportant, and need no further mention here.

We have next to consider the methods by which manganese dioxide may be made to yield the higher manganese compounds. All that is necessary is to treat it with sufficiently powerful oxidizing agents. In fact, we may even start with a manganous salt and by taking proper means go at once to the highest compounds. We will leave this for the laboratory work, and consider only the use of manganese dioxide in making the more highly oxidized compounds.

The best method is to heat together a mixture of solid sodic or potassic hydroxide, manganese dioxide, and some substance which readily yields oxygen on heating, like potassic nitrate or potassic chlorate. When this mixture is heated to fusion for a while there is formed *sodic or potassic manganate*, Na_2MnO_4 or K_2MnO_4. The reaction in its simplest form is not hard to understand. The first step is the oxidation of the MnO_2 to MnO_3, which immediately reacts with the KOH or NaOH, thus:

$$MnO_2 + O + 2KOH = K_2MnO_4 + H_2O.$$

These reactions are exactly analogous to those involved in passing from sulphurous oxide to potassic sulphate.

The product in this case is a green mass which dissolves in water to a very deep-green solution, which is fairly stable if some extra alkali be present, but which is rapidly decomposed on boiling, or by a trace of acid, with formation of *potassic permanganate*, $KMnO_4$. The reaction we will not attempt to follow. This salt, which is very stable and beautifully crystalline, has a fine reddish-purple color, and its water solution is the same color. There are a number of these permanganates known, and they all have the same color. The manganates, too, are all green, like sodic manganate.

The permanganates are of considerable importance on account of their powerful oxidizing action. In contact with any solution or any substance which is acted upon by oxygen the permanganates decompose, giving up oxygen and leaving lower hydroxides of manganese, which are usually related to MnO_2 or Mn_2O_3. This fact makes potassic permanganate a valuable *disinfectant* and a valuable oxidizing agent in the laboratory. If the solution in which the oxidation is performed contains a strong acid, the manganous salt of the acid is the final product. We will follow out these matters in the laboratory.

The atomic weight of manganese is closely 55.

CHROMIUM.

Its source is the so-called *chrome iron* ore, which is a compound of iron, chromium, and oxygen, containing about 55% of chromic oxide. It is reduced in blast-furnaces as iron is, and yields an alloy of iron and chromium called *ferro-chrome*, which is used in making the *chrome steels.*

Chromium forms the following oxides:

CrO, *Chromous oxide*	A weakly basic oxide; salts less stable than the manganous salts.
Cr_2O_3, *Chromic oxide*	A basic oxide forming salts which are rather more stable than the ferric salts, and much more so than the manganic salts.
CrO_3, *Chromic trioxide,* or *Chromic anhydride* . . .	A strong acid-forming oxide.

The oxide contained in chrome iron ore is chromic oxide, Cr_2O_3. When pure it is a green powder, which is sparingly soluble in acids.

The metal chromium itself is rarely seen. It can be obtained by reducing the oxide with charcoal, or by electrolysis of a solution of chromic chloride under carefully regulated conditions. The metal is like iron in appearance, but is much harder and more infusible. Chrome steel is very hard and tough, and is used in making projectiles for heavy guns and for lathe cutting-tools for heavy work.

The starting-point in making the chromium compounds is chromic oxide as it exists in chrome iron ore; and we will now follow out its use in preparing some of the important chromium compounds.

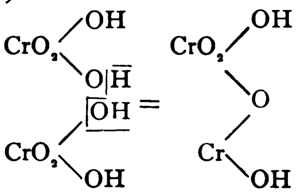
The chromous compounds are unimportant. The chromic salts are best made from the higher compounds, so the best way to begin will be with the preparation of these higher compounds.

When chrome iron ore is fused with an oxidizing agent (like KNO_3) and an alkali, the same kind of reaction takes place as we encountered in case of manganese. The chromic oxide is oxidized to *chromic anhydride*, CrO_3, which at once reacts with the alkali:

$$2Cr_2O_3 + 3O_2 + 8KOH = 4K_2CrO_4 + 4H_2O.$$

The salt formed is *potassic chromate*, and it is analogous in formula to potassic sulphate and potassic manganate. It is a bright-yellow soluble salt, stable and well crystallized. When added to metallic solutions it gives *chromates* of the metals analogous to the sulphates, and which are usually yellow.

The Bichromates, or Dichromates.—When the chromates are treated with acids *we do not obtain the acid H_2CrO_4*, but we have in solution another chromium acid called *bichromic acid*, whose salts are called *bichromates*. It is related to chromic acid thus (it being understood that there is good evidence that chromic acid is constituted the same as sulphuric acid):



or $H_2Cr_2O_7$.

This is the same kind of action discussed in connection with boric acid. The salts of this new acid are exceedingly stable, and one of them is very important.

We can pass from potassic chromate to the bichromates by adding just acid enough to remove one molecule of K_2O, and conversely we can pass back to the chromate again by adding to the solution of the bichromate just enough potassic hydroxide to add one molecule of K_2O for every two molecules of the bichromate. It is used in dyeing, and in the laboratory as an oxidizing agent. When it is heated with acids in contact with oxidizable substances, in solution or otherwise, it gives up oxygen and passes to a chromic salt of whatever acid is present. Strong hydrochloric acid breaks it down thus:

$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2.$$

Among the chromic salts only one is important, and that is the so-called *chrome alum*. Note that the formula of chromic oxide is like that of aluminic oxide. Metals whose oxides have the general formula X_2O_3 are apt to form double sulphates like common alum. And the chromium potassium sulphate,

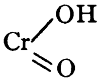
$$K_2Cr_2(SO_4)_4 + 24H_2O \text{ or } KCr(SO_4)_2 + 12H_2O,$$

is easily prepared, stable, and important. It is made by reducing potassic dichromate with sulphuric acid and some reducing agent like sulphurous acid, oxalic acid, or alcohol.

It is used as a mordant in dyeing.

The chromic salts are either green or violet. After long boiling they are always green.

We can now see how much both manganese and chromium are like sulphur in their acid-forming oxides. But it is also easy to see strong points of resemblance to iron and aluminum. For example, chromic hydroxide dissolves in cold alkalies, forming salts analogous to the aluminates, and called the chromites. Some of these chromites are apparently derived from an hydroxide,



or $HCrO_2$.

Chrome iron ore is believed to be the ferrous salt of this acid.

It is interesting to note, finally, that these salts, the manganates and chromates, which are so clearly analogous to the sulphates, crystallize, as a rule, in the same form as the sulphates.

LABORATORY WORK.

MANGANESE.

In an iron crucible melt about 5 grams KOH and 2 grams KNO_3. Add slowly 5 grams powdered MnO_2. Heat until the whole is quiet and well melted. Cool. Treat the contents of the crucible with water. Filter through glass-wool, asbestos, or sand. (Why not through paper?) Boil some of the solution. Note changes. Pass CO_2 through another portion. Add a drop of hydrochloric or sulphuric acid to another portion.

Take a little solution of pure potassic permanganate (which will be furnished), add some dilute sulphuric acid and boil. Is there any change? Put in the stick of a match and boil again. What happens? To another portion add a little sulphuric acid and then small crystals of sodic sulphite. What happens? What is being done to the sodic sulphite? Acidify another portion and pass H_2S through it for some time. What happens? Boil, filter, and test the solution for a sulphate.

Acidify a solution of ferrous sulphate, add drop by drop $KMnO_4$ solution. What happens? What is the explanation? Keep on adding and see whether there is any stopping-place. Is your solution still ferrous?

The use of manganese dioxide in making chlorine will be taken up under chlorine.

Preparation and Purification of Manganous Chloride.—Dissolve 10 grams manganese dioxide in the smallest possible amount of strong hydrochloric acid (under the hood or in the open air). The main impurity is ferric chloride. A very excellent way to get rid of this is the following: Take about one fifth of your solution and convert it into manganous carbonate. (How will you do this? Write reaction.) Wash the carbonate several times with hot water. Then scrape it from the filter-paper into the manganous chloride solution, which should have been diluted with its own bulk of water. Heat to boiling and filter. Test the filtrate for iron, by adding to a small portion a drop of potassic sulphocyanide, which gives a pink color with dilute ferric solutions, and a blood-red one with strong solutions.

CHROMIUM COMPOUNDS.

Although potassic chromate can be prepared by a method similar to that just used in making potassic manganate, it will hardly be worth while.

Conversion of Chromates into Bichromates.—Start with potassic chromate crystals, which will be furnished. Weigh out 5 grams; calculate a quantity of strong hydrochloric acid which will give one molecule of hydrochloric acid for each molecule of potassic chromate.* Dissolve the chromate in the least possible amount of water and add the acid. What happens? Write the reaction. In what respect does the new substance differ from the old? Pour off the solution. Redissolve the crystals in a little water; set the solution aside and allow it to crystallize slowly so as to get larger crystals.

Conversion of Bichromates back to Chromates.—Weigh 5 grams $K_2Cr_2O_7$. Calculate the quantity of solid KOH necessary to give one molecule K_2O to each molecule of $K_2Cr_2O_7$. Weigh out the calculated amount and mix the two substances. Evapoate and crystallize out the chromate.

Acidify small portions of a solution of $K_2Cr_2O_7$ with dilute sulphuric acid and boil. Try now the effect of various reducing substances as you did with potassic permanganate, and record your result. In so far as you understand what is taking place in each case, state it in your notes.

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* The strong acid may be assumed to contain about 37% HCl.

Try the action of $K_2Cr_2O_7$ on an acidified solution of ferrous sulphate just as you did with potassic permanganate.

Chromic Anhydride.—Make 20 c.c. of a strong solution of potassic dichromate. Cool. Add to the solution twice its volume of concentrated sulphuric acid. The fine, red needle-like crystals which separate consist of CrO_3. It can be collected on a glass-wool or sand filter, but it is hard to dry unless all the sulphuric acid is thoroughly sucked out of it by the aspirator. It is hardly worth while to do more than precipitate it and note its appearance.

Preparation of Chromic Chloride.—The best method is by reducing a solution of potassic dichromate (use 5 grams) with H_2S. It would be naturally expected that we should get Cr_2S_3 by this process, but chromium does not form stable salts with the weak acids, and the sulphide is immediately decomposed by water with formation of the hydroxide and evolution of H_2S:

1. $K_2Cr_2O_7 + 7H_2S = K_2S + Cr_2S_3 + S_3 + 7H_2O$.
2. $Cr_2S_3 + 6H_2O = 2Cr(OH)_3 + 3H_2S$.

The chromic hydroxide is now to be filtered, washed, dissolved in HCl (the sulphur remaining undissolved) and the solution evaporated carefully. When it is at quite small bulk take out half into another dish and let it stand and evaporate slowly. Dry the other half carefully over the lamp. Note the different colors of the two lots. Devise another method for making chromic chloride from potassic chromate.

Some Other Metallic Chromates.—Add small portions of a solution of K_2CrO_4 to the following metallic solutions:

Argentic nitrate,	$AgNO_3$;
Plumbic nitrate,	$Pb(NO_3)_2$;
Baric chloride,	$BaCl_2$;
Cupric sulphate,	$CuSO_4$.

The precipitates are the chromates. Note colors and write reactions.

TESTS FOR MANGANESE AND CHROMIUM.

Chromium compounds when melted into a borax-bead, color it green. Manganese compounds color the bead amethyst-purple when the bead is heated in the outer portions of the flame. On heating the bead in the inner portions of the flame the bead becomes colorless. Try the tests.

INTRODUCTION TO THE STUDY OF COPPER, SILVER, GOLD.

THESE metals are located, by the Mendelèeff table, in the same general group with sodium, potassium, lithium, etc. Their resemblance to these elements is, however, confined to analogies between certain of their compounds. The metals themselves in their appearance, texture, and mode of occurrence are sharply separated from the sodium metals. For example, all three of them are found free in nature; gold exclusively so. They do not decompose water at a red heat. Silver and copper are typically metallic in their chemical behavior, while gold shows in some of its compounds a feeble acid-forming tendency. Gold and silver are not in the least attacked by oxygen or by moist air even at high temperatures. Copper is readily attacked by oxygen at a dull-red heat and is rapidly corroded by moist air. On the other hand, each forms a series of compounds in which the valence of the metal is one, and these salts often crystallize in the same forms as the corresponding sodium and potassium salts. The specific gravities and (approximate) melting-points of the metals are:

	Specific Gravity.	Melting-point.
Copper	8.94	1045°
Silver	10.55	954°
Gold	19.03	1200°

LABORATORY WORK.

Try the action of the three dilute acids (both hot and cold) upon copper.

Try also the action of sodic hydroxide and lastly of ammonium hydroxide. In this latter case make two experiments. First take a short piece of tubing about ¼ inch outside diameter and 4 or 5 inches long. Seal one end ; put in a piece of clean, bright copper wire. Nearly fill the tube with strong ammonia solution and stop it up *air-tight* (by putting in a piece of rubber tubing as a sleeve and then a piece of glass rod). Now take another similar piece of tubing; put in a piece of copper wire about 2 inches long and pour in ammonia until the wire is under the liquid. Set the two tubes away and allow them to stand for some time. Note the appearance from time to time.

Place in your 100 c.c. flask about five grams of copper filings or fine turnings wet with dilute sulphuric acid. Turn and shake the flask so as to distribute the turnings well over the interior walls. Set the flask in an inverted position with its mouth dipping under water. Allow it to stand overnight. Has any copper passed into solution ? What is the gas remaining in the flask ? What is generally the nature of the reaction when metals dissolve in dilute sulphuric acid ? What difference is there in this case ?

The action of nitric acid upon copper has already been studied.*

We have already made the acquaintance of cupric oxide. Heat a strip of sheet copper to a red heat in the extreme upper part of a good Bunsen lamp and see how easily the copper oxidizes. By what other methods could the oxide be made ? See if ammonia will dissolve it.

Cupric Hydroxide.—To a solution of cupric sulphate add sodic hydroxide. Note the color. Then add more sodic hydroxide and boil. What change in appearance takes place ? What does the precipitate suggest by its appearance ?

Add ammonic hydroxide very slowly to solutions of cupric nitrate, cupric sulphate, and cupric chloride.

Try the action of the above named cupric salts upon litmus (the salts being in water solution).

Cupric Bromide.—Prepare this salt by placing about five drops of liquid bromine in a small test-tube, adding about five times its volume of water, and a piece of copper wire an inch or so long.

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* See p. 245. For the behavior of cupric nitrate when heated, see p. 254.

Warm the whole *very gently* (under the hood). Action takes place; and in a few minutes the copper is all converted into the bromide. The solution is now to be boiled down (*under the hood*) to small bulk to drive off the extra bromine. Then add a drop of strong hydrobromic acid (HBr). The solution will now be dark purple. Gradually dilute it with water and notice the color changes. When the color is finally light blue, add a little of the strong hydrobromic acid again. What takes place?

According to the dissociation theory the color of a solution containing an acid, a base, or a salt is determined either by the color of the ions or by the color of the undissociated molecules. The ions of the cupric bromide solution are the cupric ion and the bromine ion. All the cupric salts when in dilute water solution (and consequently very highly dissociated) have the same faint blue color which appears to be due to the color of the cupric ion. A very concentrated solution of cupric bromide is only partially dissociated, and if we add a drop of hydrobromic acid the dissociation is still further diminished.* The color of the solution is, under these circumstances, due to the color of the undissociated molecule. The color change on diluting is easily understood from this point of view. And when finally we add strong hydrobromic acid to the dilute solution it may be seen how the strongly dissociated acid acts to diminish the dissociation and increase the number of undissociated molecules, the color of the solution changing correspondingly.

Effect of Deoxidizing Agents upon Cupric Compounds.—1. To about 20 c.c. of a cupric sulphate solution add a little dilute sulphuric acid and a strip of zinc. Note carefully the appearance of what separates on the zinc. Does the solution change color? When the zinc is all gone and the solution colorless, filter; save the filtrate. Lay a little of the precipitate on the desk and press it strongly with a knife-blade. Put some in a test-tube and treat it with a few drops of dilute nitric acid. Put some into a slightly acid (HCl) solution of $HgCl_2$.†

What does the substance suggest by its properties?

Take now the colorless solution from which the precipitate was separated by filtration. Evaporate some carefully to dryness, and test the residue for zinc. Is there any doubt as to what acid ion was present in the solution? What now would be your explanation of what has taken place between the zinc and the cupric sulphate? Does it suggest any way of getting at the atomic weight of copper? See if you can devise a method.

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* See p. 195.

† See p. 346.

2. *Cuprous Chloride.*—Make about 10 c.c. of a strong water solution of cupric chloride. Add to it a very strong solution of primary sodic sulphite ($NaHSO_3$), or else, if more convenient, saturate the solution with sulphurous oxide, which can be generated in a 100 c.c. flask by heating some small bundles of copper wire with about 10 c.c. of strong sulphuric acid, or else (and better) by putting about 25 c.c. of strong sodic sulphite solution into a flask provided with funnel-tube and delivery-tube so arranged that the gas can be passed through the solution of cupric chloride, and then pouring strong sulphuric acid, a few drops at a time, down the funnel-tube, when sulphurous oxide will be evolved. What visible effects are produced upon the solution? When there is no further change, pour the solution into about 100 c.c. of water. Let it settle. Pour off the solution. Pour more water over the residue, let it settle and pour off again. Repeat this process once more. Filter and wash once or twice with water.

Take some of the moist residue and spread it out in a thin layer on a piece of filter-paper; expose it to the air. Dissolve a little in dilute nitric acid. See if you can satisfy yourself as to what the substance is. For what acid ion will you test? Dissolve a little more in strong hydrochloric acid and add a little hydrogen dioxide, or some other oxidizing agent.

To a water solution of glucose* (grape-sugar), which acts as a reducing agent, add cupric sulphate (strong solution). Boil, and add slowly sodic hydroxide, keeping up the boiling. When no further change is seen, filter and wash several times with hot water. Try some of the precipitate with dilute nitric acid. Stir it up with a drop or two of mercury moistened with HCl. Press it under the knife-blade. Is it metallic copper? What does the evidence indicate? Put some in your porcelain crucible and heat it. What takes place? Putting together all you have seen of the behavior of the substance, what does it suggest to your mind?

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* If this is not available, boil a few c.c. of a solution of white sugar with a few drops of strong hydrochloric acid. This solution will do for the above experiments.

SILVER COMPOUNDS.

Argentic Nitrate.—Dissolve a small fragment of metallic silver in dilute nitric acid. Evaporate and heat the residue *very gently* until it melts. Cool; dissolve in water and try the action of litmus. Divide the solution into three parts.

Argentic Chloride, Argentic Bromide and Argentic Iodide.—To one portion of the solution just prepared add sodic chloride, to another potassic bromide, and to the third potassic iodide. Compare the colors. Divide the contents of each tube into three parts. Try the following tests in each case: 1. Set some of the mixture in bright sunlight.and see if the color is changed. 2. Try the effect of adding some strong ammonia. 3. Try adding a strong solution of sodic thiosulphate, $Na_2S_2O_3$ (often called "hyposulphite of soda" or "hypo") Keep careful notes.

Argentic Oxide.—Add sodic hydroxide to a solution of argentic nitrate; boil. The precipitate is not argentic hydroxide *after boiling*. It probably is largely so before it is boiled (compare the behavior of cupric hydroxide). Filter it, wash carefully with hot water and dry at a temperature below 100°.

Action of Copper and Zinc upon Silver Solutions.—Take two small portions of argentic nitrate solution. Add to one a bright strip of zinc, to the other a bright strip of copper. Can you study out what happens, and bring evidence? Try.

Atomic Weight of Silver.—Three methods are available. One of them is suggested by the last experiment. A second consists in determining composition of the chloride, and the third consists in determining the composition of the oxide, which we can do since it decomposes easily, on heating, into oxygen and silver (like mercuric oxide, only much more easily).

Select one of these methods, plan all the details with the best judgment you can bring to bear, and calculate your results. The specific heat of silver (which will be given you) will enable you to settle the question of the valence of silver in the compounds studied.

LECTURE 57.

COPPER, SILVER, AND GOLD.

Copper is found in the metallic state, near Lake Superior, in enormous quantities, and as might be expected its compounds are found quite abundantly in the same localities; particularly the black cupric oxide (melaconite), the red cuprous oxide (cuprite), the carbonate (malachite), and *copper pyrites*, which is a sulphide of iron and copper.

The process of extracting metallic copper from its ores is simple or complex, according to the ore. In case of the native metal, all that is necessary is to "refine" it. The oxide ores are simply heated in moderate-sized blast-furnaces with coal, coke, or charcoal. The carbonate is first "roasted" to convert it into oxide, then reduced as just described. The ores containing sulphur are the really troublesome ones. The reduction process in this case consists of a series of alternate roastings in the air and meltings with rich slags from previous operations, pure metal being finally reached only after considerable pretty careful work. In any case the metal has to be "toughened." This is done by melting it and stirring the melted metal with a pole of green * wood, until a sample cast into an ingot, "nicked" and broken, shows the right kind of a fracture.

Copper forms two oxides and two series of compounds. In the cupric compounds its valence is two. As to the cuprous series there is some difference of opinion. As usual, the real "bone of contention" is the chloride. There is no question but that there are the same number of copper as of chlorine atoms in the molecule; but some think the formula of the chloride is CuCl, and some think it is Cu_2Cl_2. Those who hold the latter view think that the valence is the same in one series as in the other, and that the molecule of cuprous chloride is made up thus:

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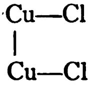
* The object of this process is to remove from the melted metal dissolved cuprous oxide, which would make it brittle. This is accomplished by the reducing gases given off by the wood when it is heated. Green wood is best since it gives more gases than does dry wood.

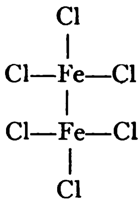


$$\begin{array}{l} \text{Cu}—\text{Cl} \\ \mid \\ \text{Cu}—\text{Cl} \end{array}$$

Those who hold for the simpler formula believe that the valence is *one* and that the molecule is constituted like that of sodic chloride,

$$\text{Cu}—\text{Cl}.$$

Exactly the same style of controversy prevails with reference to several other metallic chlorides whose molecular weights are hard to get at experimentally. Mercurous chloride is a case similar to cuprous chloride. In case of ferric, aluminic, manganic, and chromic chlorides, each of which is admitted by all to contain three times as many chlorine as metal atoms, some think the valence of the metal is *three*, and the formula of the chloride in general XCl_3; others think that the valence is *four*, and that the molecules are in general X_2Cl_6, being made up as shown below, where ferric chloride is taken as an illustration.



$$\begin{array}{c} \text{Cl} \\ \mid \\ \text{Cl}—\text{Fe}—\text{Cl} \\ \mid \\ \text{Cl}—\text{Fe}—\text{Cl} \\ \mid \\ \text{Cl} \end{array}$$

The molecular weight determinations present great difficulties, and it is impossible to come to a decided conclusion in the present state of the experimental evidence. It may be said, however, that one formula will serve all our ordinary purposes as well as the other, and that there is no fact known at present of such a character as to prohibit the use of the simpler formula.

CUPROUS COMPOUNDS.

Cuprous oxide is formed, as has been seen in the laboratory, when cupric hydroxide is precipitated under strongly reducing conditions. Grape-sugar, glucose, and cane-sugar which has been boiled with dilute acids are good reducers in this case. It is a red powder, which is easily changed by heat into cupric oxide.

Cuprous chloride may be made as it was in the laboratory or by boiling a solution of cupric chloride in strong hydrochloric acid with excess of copper turnings or gauze, and pouring the solution into water (since the chloride is sparingly soluble in water, though soluble in strong HCl).* Its ammonia solution absorbs oxygen from the air very rapidly, and is sometimes used to absorb oxygen in analyzing gas mixtures.† Notice that this chloride of copper, which has the same formula as argentic chloride, resembles it, as it does also mercurous chloride, in being sparingly soluble in water.

CUPRIC COMPOUNDS.

Cupric oxide is well enough known to us by our past experience with it.

The most of the other cupric compounds are of little consequence. We will consider only two or three.

Cupric sulphate is a rather important salt. It is sometimes found occurring naturally, having been evidently formed by the oxidation of copper pyrites in presence of water. It is sometimes made by roasting poor ores of copper containing sulphides, which are thus converted into the sulphate, and this, being soluble in water, is easily extracted. At this stage we do not need to inquire by what methods the salt can be made in the laboratory, as the methods are the same as for any salt; but one reaction will be mentioned, since it is quite an interesting one.

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* Compare this method with that used in making mercu*rous* nitrate and fer*rous* sulphate.

† This can be easily tried in the laboratory if desired.

Copper, as we have seen, dissolves in dilute sulphuric acid very slowly in contact with the air at ordinary temperatures. Even when the acid is boiled it dissolves only very slowly. Cold concentrated sulphuric acid has no action, but when the strong acid is *heated* with copper, *sulphurous oxide comes off*, and cupric sulphate passes into solution. (See under Compounds of Sulphur.)

The facts above stated can be expressed thus:

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2;$$

but there could hardly be a better text for a sermon on the much that usually remains untold when we have complacently "written the reaction." In this particular case the most superficial examination of the flask and its contents will show other products of the reaction never hinted at in the reaction above written. And as for the question *how* the reaction is brought about—that is an open question to-day. It is clear that the sulphuric acid is reduced, *but by what?* It is a question very much like that we encountered in dealing with the action of nitric acid upon copper (see p. 245).

Cupric sulphate is a very beautiful blue salt. It can be easily recrystallized from water, since it is much more soluble in hot than in cold water. It crystallizes with five molecules of crystal-water, four of which go off on heating to 100°; the fifth only goes off at about 250°, hence it is probably held in the molecule differently from the rest; but how it is held, or how the rest are, or how crystal water generally is held by salts and other substances is not known.

The salt is called *blue vitriol*, and has a variety of uses.

Some of the insoluble copper salts are green, and are used as pigments or paints. Cupric sulphate is the starting-point used in the preparation of these. It is also used in copper-plating and in some forms of galvanic-battery cells.

The copper salts are, in general, poisonous. Since this is so, and since our laboratory work shows that weak acids like acetic acid (the acid of vinegar) and even carbonic acid *in contact with air* act upon copper (as shown by the fact that the green "rust" on copper which has been exposed to moist air is a basic *carbonate* of copper), it follows that copper is not a good material for cooking utensils, especially if the substances boiled in them contain vegetable acids, although these may be very weak.

Uses of the metal copper will be easily called to mind. One of the most important uses, for electroplating and electrotyping, will be considered in another connection.

When copper and zinc or tin are melted together we get *alloys* called *brass* and *bronze*, respectively. The uses of these alloys are very numerous.

SILVER.

Some is found *native* (or free). Some in the form of the sulphide Ag_2S (argentite). Small quantities of the chloride are occasionally found. The naturally occurring argentic chloride is called *horn-silver*, because it has much the appearance and consistency of horn. Some other ores occur which are pretty complicated mixtures of argentic sulphide with the sulphides of lead, arsenic, copper, etc., and whose treatment will not be considered here. The reduction of the simple ores is easy and presents no new features. Some of the poorer ores are roasted with salt, yielding argentic chloride, which is then reduced by contact with metallic iron in presence of water, ferrous chloride being formed.

A great deal of silver is obtained in the course of extracting metallic lead. These processes will be dealt with in connection with lead. The metal has many uses. Its value depends mainly upon two things: the slight extent to which it is corroded by air either moist or dry, and its fine lustre. The pure metal, however, is too soft for most purposes, and it is usually "alloyed" with copper. The United States coin-silver contains 90% silver and 10% copper. "Sterling" silver contains 92.5% silver and 7.5% copper.

The metal dissolves in nitric acid and in hot concentrated sulphuric acid (like copper, and with the same gaseous product). It is also dissolved by ammonia as copper is, *in contact with the air or oxygen.* Nearly pure silver can be prepared in the laboratory by several processes. One consists in preparing and washing silver chloride (starting with, say, coin-silver) and reducing this to metal by boiling it with sodic hydroxide and milk-sugar, grape-sugar, or cane-sugar which has been boiled with dilute acid. Other methods may be found in larger works.

When ammonia solutions of argentic nitrate are heated with certain reducing agents under carefully regulated conditions in clean glass vessels, or in contact with any clean glass surface, the silver is deposited as a smooth, coherent, brilliant coating upon the glass. This fact is turned to account in silvering mirrors for use in reflecting telescopes. The process is, however, one which requires care and intelligence, for under certain circumstances a very dangerously explosive silver compound is formed, and serious accidents are on record from this cause.

Argentic Oxide.—Most of the important points have been brought out in the laboratory. It is worth noticing that it is a strongly basic oxide and forms neutral salts with the strong acids. It is slightly soluble in water, and its solution is decidedly alkaline. It dissolves readily in ammonia. The solution on slow evaporation sometimes deposits a black, explosive compound of silver, oxygen, and ammonia. It is best not to have much to do with the ammonia silver solutions.

Argentic chloride, bromide, and iodide are interesting on account of their insolubility, and on account of their behavior in sunlight. They are all affected more or less, even though the exposure be brief, and one of the effects is that after the exposure they are more easily acted upon and reduced to metal by some reducing agents than they were before. This is the fundamental fact of photography.

A glass plate is coated with gelatine which has been impregnated with, say, argentic chloride. The "camera" has a "shutter" by which the light can be admitted when desired, and a system of lenses by which the image of whatever is in front is focused on the gelatine plate when the shutter is opened. The exposure is made long or short according to the nature of the plate, and the state of the light at the time of exposure. The plate is naturally most affected where the light portions of the image come, the perfectly dark parts being not affected at all. The plate is then carried into the dark room and treated with a "developer," which is simply *a reducing agent that in the cold will not affect plain argentic chloride, but will reduce it after it has been exposed to the action of light.* The final effect, then, is to reduce the argentic chloride on those portions of the plate where light has been. Next, the plate is washed and the unchanged silver chloride is dissolved off by sodic thiosulphate which forms a *soluble* double thiosulphate of silver and sodium:

$$Na_2S_2O_3 + AgCl = NaCl + NaAgS_2O_3.$$

This leaves the picture, drawn in lines of silver, on the glass; but the trouble is that portions of the picture which are dark are really the ones that were *light* in the original image. To get a truthful picture we take paper which has been saturated with argentic chloride and dried, and putting the negative tightly against it in a "printing-frame," expose the whole to sunlight. The silver chloride is darkened where the light strikes through, but not where the dark lines are, and as a result we obtain a "print" in which the light and dark are rightly distributed.

There are countless details both in the making of negatives and in printing; but they cannot be considered here.

Most of the silver compounds dissolve in ammonia and in potassic cyanide. A solution of argentic cyanide in potassic cyanide (containing, of course, a double salt) is used in *silver-plating*, which will be taken up presently.

GOLD.

The general facts as to the occurrence of gold and its extraction are so well known that it is only necessary to say that the metal is sometimes found in lumps of different sizes, or as "dust" or "nuggets," mostly in old river-beds and sometimes in veins in quartz. The only considerable reservoir of gold compounds is the ocean, which contains something less than one grain of gold per ton. The quantity of gold thus represented is greater than that available from all other known sources put together; but thus far it is practically inaccessible, no economical method of extraction being known. Native gold usually contains silver and sometimes platinum and other metals in small quantities. California, Alaska, South Africa, and parts of Siberia are the main localities where gold is found in quantity, but it is present in traces almost everywhere.

Nearly pure gold can be made in the laboratory very easily. Gold solutions are reduced to metal by most reducing agents, such as sulphurous oxide, ferrous sulphate, or oxalic acid. The gold usually precipitates in very fine powder, and if the solution is dilute the powder is purple. On heating it assumes its regular yellow color. It is unacted upon by any of the acids except a mixture of concentrated nitric and hydrochloric acids, which is hence called *aqua regia*, because it will dissolve the royal metal. The gold is converted into its chloride by this mixture, and the same is true of any metal which is attacked by it. Its power lies in the fact that nitric and hydrochloric acids when heated together decompose each other and yield, among other things, either free chlorine or unstable compounds rich in chlorine, which give up their chlorine to the metal.

Gold is rarely used pure. It is too soft. The alloy used in coins in this country contains 90% gold and 10% copper. This alloy is harder than pure gold and a little darker in color.

Gold used for jewelry is also alloyed with copper. The various alloys are designated by a rather awkward arbitrary system, in which pure gold is called *24-carat gold.* The alloys are then designated as 14-carat, 18-carat, etc., *according to the number of parts pure gold in 24 parts of the alloy.*

Thus, 18-carat gold contains 18 parts gold, 6 parts copper in 24 parts.

Gold-leaf is gold which has been beaten out into very thin sheets.

No particular mention will be made of the compounds of gold, as they are few and not specially important. It forms salts with only hydrochloric, hydrobromic, and hydriodic acids. It forms three chlorides $AuCl$, $AuCl_2$, and $AuCl_3$. The hydroxide $Au(OH)_3$ behaves toward the alkalies as $Al(OH)_3$ does, *i.e.* as a weak acid, and forms the *aurates.*

Precipitation of Metals on other Metallic Surfaces—Electroplating.—It will be remembered that we have come across several reactions in which, by introducing a metal into a solution of some salt of another metal, a second metal separates out in the free state, while the first metal passes into solution. Thus when zinc is placed in a solution of cupric sulphate the zinc slowly disappears and the copper appears as metal. Similarly when copper is put into a solution of argentic nitrate the silver separates as metal and the copper passes into solution. To confine ourselves to the cases before us, either zinc or copper will precipitate metallic-silver from a solution of one of its salts, but silver will not precipitate zinc, and neither will copper. If we were to carry our studies further and make similar experiments, involving all the ordinary metals, we should find ourselves confronted with an array of similar facts. In order to see how these facts can be put in a form that will be easily grasped, let us once more look at zinc, copper, and silver. If we arrange the three metals thus:

Zinc,
Copper,
Silver;

that is, if we so arrange them that those metals which experience shows are precipitated from solutions of their salts by a given metal—zinc, for example—are written beneath that metal, then in the case of zinc, copper, and silver the order is as above given. Now extensive experiments have been made in this line; and the result has been to extend considerably the little "precipitation series" given above. Excluding those metals which decompose water at ordinary temperatures we should have

Magnesium,
Zinc,
Iron,
Lead,
Tin,
Bismuth,
Copper,
Mercury,
Silver,
Platinum,
Gold.

This table leaves out some of the less important metals. It is true only for the particular case above stated—that is, when the metal in question is immersed in a solution containing a salt of the other metal. With this understanding it is true that any metal in this table will precipitate any one of those below it.

Turn now for a moment to another order of facts. We have seen how solutions of some metallic salts behave when the galvanic current is passed through them. A good example is cupric sulphate. When this is electrolyzed, metallic copper separates at the negative electrode, while the SO_4 ion gives up its charge at the positive electrode and forms sulphuric acid with the water of the solution. At present all we are interested in is the metal end of the line. In the first place, it is a fact of great practical importance that by electrolyzing suitable salts of certain metals, notably silver, gold, nickel, and copper, the negative electrode being almost any metallic object with a smooth, clean surface, the metal in solution is deposited upon the electrode in a thin, compact film, which can be polished or burnished. This fact underlies all the so-called *electroplating* processes.

What now would happen if we were to take a solution containing salts of all the metals given above, and pass a galvanic current through the solution? Would all the metals begin to separate at once? Here, again, experiment is the only means of getting an answer; and experiment shows that if we begin with a very low electromotive force or "voltage" and gradually increase it, no one of the metals in solution will separate until the electromotive force rises to a certain value. When it reaches this value certain metals begin to separate out on the negative electrode, and as the voltage is slowly increased, one metal after the other separates. Indeed, it looks as though with a suitable solution and very carefully graduated current we ought to be able to separate each metal quantitatively before the next one came, and *to a certain extent* this can be practically realized. If now we should once more make a table, putting at the bottom the metal that separated first, and adding the others in the order in which they come out, *we should obtain the same table as the one above given.*

This is a very striking fact, and we can hardly avoid the conclusion that the two sets of experiments are closely related to each other, and are manifestations of the same fundamental relation between the metals concerned.

Moreover, if we recall the picture of the process of electrolysis as presented to us by the dissociation theory, the first glimmering of a possible explanation appears. Suppose we have our mixture of metallic salts in a decomposing-cell with the two electrodes dipping into it. One of the electrodes is maintained positively charged, the other negatively, by a battery or some other source of electricity. In solution we have the positively charged metal ions, and the negatively charged acid ions; and these are attracted, each by the oppositely charged electrode. *Now, it almost seems as if there was a difference in the ease with which the metal ions give up their charges to the electrode.** It may be that this is the case, and that the metals that come out first are those that give up their charges the most easily.

The application of this hypothesis to the case where one metal is precipitated by another is rather more difficult to follow; but it may be said that everything at present known seems to indicate that the whole matter is an electrical one, and not a question of the relative "affinities" of the metal ions for the acid ion in solution.

According to the view we are now discussing, the difference between the metals consists in the different intensity of their electric charges as ions, and the top members of the table are, accordingly, the most strongly electropositive metals, at least under the circumstances above specified.

When two metals are brought into a liquid, say dilute sulphuric acid, the metal plates being connected by a wire, it can be shown that an electric current sets up in the wire and flows from the less to the more electropositive metal. This fact underlies all the numerous forms of the galvanic battery. The simplest is the common "Daniell cell." In this the two metals are copper and zinc; and each one stands in a solution of its own sulphate, the two solutions being in contact with each other. When the zinc and copper plates are connected by a wire, the zinc passes slowly into solution. The copper, on the other hand, *separates out*, so that after a long time the zinc plate is all dissolved, while the copper has gained in weight from the deposited copper. Moreover, experiment shows that for every 65 grams of zinc dissolved 63.6 grams copper separate on the copper plate; which means, of course, that for every atom of zinc that passes into solution an atom of copper separates from the solution.

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* See Le Blanc's *Electrochemistry*, p. 264.

This is one of the simplest cases, and yet anything like a discussion of it would fill many chapters of this book. Within a very few years some progress has been made toward an understanding of the matter, and it is quite possible that before this book is "out of print" some of the results will be sufficiently well established and clear, to warrant more extended consideration in its pages than can now be given. Suffice it to say that the key to the whole matter seems to be *the electrical behavior of the metal ions.* The dissociation theory once more shows its usefulness.

Finally, if we should make and test a number of cells like the Daniell cell, using metals other than zinc and copper (each metal, of course, standing in a solution of one of its salts), we could construct a table in which the metals *from which* the current flows in the wire are written beneath those *to which* the current flows. *We should once more come out with the same table as in the other two cases.*

One or two points in connection with electroplating are of special interest from the standpoint of the dissociation theory.

In plating with copper it is a comparatively simple matter to get a smooth, coherent coating; and the solution employed is simply a solution of cupric sulphate. In plating with silver, gold, or nickel, however, it is not found possible to obtain coherent films unless the rate of deposition be very carefully regulated. The two controlling factors here are the current strength and the concentration of the silver ions; both these must be kept as nearly constant as possible.

The regulation of the current is not difficult; but it is not, at first sight, so easy to keep the concentration of the silver ions constant. Moreover, the concentration of the silver ions must be rather low. This is accomplished by using as the plating solution a solution of the double cyanide of potassium and silver, $KAg(CN)_2$, or $KCN.AgCN$.

This salt dissociates primarily into $\overset{+}{K}$ and $Ag\overset{-}{(CN)}_2$ ions. Here we have a behavior like that of the double cyanides of iron. But the ion $Ag(CN)_2$ appears to dissociate slightly into $\overset{+}{Ag}$ and $(\overset{--}{CN})_2$ ions; and the result is that when the circuit is closed at least two processes at once start up. In one of them the silver ions in solution begin to give up their charges, and deposit as a film of silver on the negative electrode (or *cathode*); while the two $\overset{-}{CN}$ ions go to the positive electrode (or *anode*), where they give up their charges. We will not follow them further. The main point is that some silver ions have left the solution, and unless the loss can be made up, the rate of deposition must change. The desired end is accomplished by the dissociation of the complex ion $Ag\overset{-}{(CN)}_2$. The anode is a plate or rod of pure silver, and as fast as a silver ion is removed from solution at the cathode a cyanogen ion takes a silver ion into solution at the anode, and thus has the effect of keeping not only the concentration of *free* silver ions constant, but also of keeping the quantity of complex silver-bearing ions constant also.

This gives a fair idea of what is believed to take place.

The same kind of a solution is used in case of gold-plating, and the results are of the same nature.

In case of nickel the double sulphate of nickel and ammonium $Ni(NH_4)_2(SO_4)_2$ is used. Here the complex ion $Ni(NH_4)_2$ is the important agent in keeping the concentration of the nickel ions constant.

THE PLATINUM METALS.

The eighth group in the table contains six metals which divide naturally, on the basis of their properties and chemical behavior, into two divisions of three each. The first division contains palladium, ruthenium, and rhodium; the second platinum, osmium, and iridium. They are all heavy, lustrous metals, which are found in "platinum ore," which contains about 50% metallic platinum, the rest being the above-named metals. The supply is not very abundant, the extraction is difficult, and some of the metals have properties that make them exceedingly valuable. All the circumstances combine to make "the platinum metals," as they are called, very expensive.

It will not be worth while to study them in detail, but their situation in the Mendeléeff table and their relations with iron, cobalt, and nickel are too interesting to pass without mention, even in an elementary survey.

This eighth group is a very peculiar one. It consists of three triads of the second class—that is, triads in which the atomic weights are very close together. The first triad contains

Iron.	Cobalt.	Nickel.
At. wt. 55.8	At. wt. 58.7	At. wt. 58.6
Sp. Gr. 7.8	Sp. Gr. 8.5	Sp. Gr. 8.8

The second,

Ruthenium.	Rhodium.	Palladium.
At. wt. 103.5 Sp. Gr. 12.26	At. wt. 104.1 Sp. Gr. 12.1	At. wt. 106.2 Sp. Gr. 11.5

The third,

Osmium.	Iridium.	Platinum.
At. wt. 191 Sp. Gr. 22.48	At. wt. 192.5 Sp. Gr. 22.42	At. wt. 194.3 Sp. Gr. 21.50

When we come to look at these triads, we find that, taken altogether, they make a little table by themselves, in which both the vertical and the horizontal rows of elements constitute natural groups. In the horizontal rows the resemblance is more of an all-round one. Iron, cobalt, and nickel are, by their mode of occurrence and their general characteristics, a pretty clearly marked group; but if we are looking for analogies in compounds, iron, ruthenium, and osmium are more strikingly alike than iron, cobalt, and nickel.

The same remarks apply to cobalt, rhodium, and iridium, and to nickel, palladium, and platinum. Only a few general statements will be made as to these relationships, and we will then briefly consider two representatives of this group, palladium and platinum.

Note, in the first place, how close the specific gravities lie to each other in the horizontal rows. Note also how these rise with rising atomic weight in the vertical series *and fall with rising atomic weight* in the second and third horizontal series.

As to the vertical series, ruthenium and osmium rival manganese in the number of oxides they form. In fact, their oxygen compounds are almost perfectly analogous to the manganese compounds. They form, however, oxides RuO_4 and

OsO_4, which show a higher valence toward oxygen than manganese ever shows. The metals themselves, moreover, can be oxidized by heating in the air or in oxygen.

Rhodium and iridium are less easily oxidized, form less oxides, and notably *no acid-forming oxides*, unlike ruthenium and osmium, which form acids exactly analogous to manganic and permanganic acids.

Palladium and platinum, which are very difficult to oxidize directly, form a still smaller variety of oxides and of compounds generally.

Passing now to the consideration of individual members, palladium is obtained from platinum ore, and also from certain gold ores. It is a white, lustrous, malleable metal, soluble in nitric and in (concentrated) sulphuric acid. It forms two chlorides, $PdCl_2$ and $PdCl_4$.

The most remarkable thing about palladium is its behavior toward hydrogen. On looking at the Mendeléeff table it will be seen that the power to form compounds with hydrogen begins decidedly at group IV and diminishes till it disappears for the most part at group VII. It will be seen, too, that if the elements of group VIII did form any hydrogen compounds, and if the power of fixing hydrogen atoms (as measured by the valence of the element in its hydrogen compounds) continued to diminish at the rate it has up to group VII, the *hydrides* of group VIII ought to have the formula X_2H.

When palladium is used as the negative electrode of a water-decomposing cell, or when hydrogen is passed over palladium heated to 100°, the metal absorbs something like 900 times its volume of the gas. The metal increases notably in bulk, and its physical properties undergo some changes. It is easy to analyze this curious substance. The hydrogen is driven off by heating and the residue is palladium only. If this be done quantitatively the substance turns out to have the formula Pd_2H, which is the formula of the anticipated hydride of palladium. Moreover, it is possible to calculate from the specific gravity of the compound and the known specific gravity of palladium the specific gravity of the *condensed hydrogen*, and this turns out to be 0.62. Since the specific gravity of liquid hydrogen has been recently found to be 0.07, it appears that the element, as contained in the palladium compound, is about nine times as dense as liquid hydrogen.

This compound, or alloy, has recently furnished a very convenient means of weighing large volumes of hydrogen without having to use large vessels to enclose it. This method was recently and very successfully employed in accurate determinations of the composition of water by weight. Finally, it is worth noticing that palladium is not the only metal that can absorb hydrogen—a number of them do, but to nothing like the extent palladium does.

Platinum is an essential metal to the modern chemist on account of its power to resist the action of all acids except a mixture of strong nitric and hydrochloric acids, and on account of its high melting-point. It is, moreover, very malleable and ductile and can be drawn into very fine wire. Dishes, crucibles, retorts, beakers, and stirring-rods are made from it, and these are used in work where it is important that the materials worked upon shall run no risk of contamination from the vessels containing them.

The metal forms no oxides directly, and those it forms by indirect means are of little importance. Like palladium, it forms two chlorides, $PtCl_2$ and $PtCl_4$. Of these only the last merits mention. It is formed when platinum is dissolved by *aqua regia.* The solution on evaporation leaves a salt carrying crystal water. If this be dissolved in hydrochloric acid, the solution does not give the ordinary reactions given by the platinum ion, and electrolysis of the solution shows, on careful study, that one of the ions is hydrogen and the other an ion *containing both platinum and potassium.* Moreover, when a solution of KCl or NH_4Cl is added, yellow crystalline salts are precipitated; and analysis shows that they contain potassium, platinum, and chlorine, the formula of the potassium salt being K_2PtCl_6. The most sensible explanation is that we are dealing with one of those double salts which in water solution form *complex ions* like the ferrocyanides and ferricyanides. Accordingly the solution of $PtCl_4$ in HCl is believed to contain a *chloroplatinic acid* H_2PtCl_6 whose salts are called the *chloroplatinates*. The potassium salt is important, because it enables us to separate potassium from sodium. Sodium chloroplatinate is easily soluble in water, while the potassium salt is rather sparingly soluble, and still less soluble in alcohol. If, therefore, we add to a solution containing potassium and sodium chlorides, chloroplatinic acid, the potassium is almost completely precipitated, especially if the solution be concentrated and if alcohol be added. The sodium compound remains in solution.

Many of the double chlorides of the metals show the same behavior noted above to a greater or less extent, and the same is true of the double bromides, iodides, fluorides, and particularly, as we have seen, the cyanides.

INTRODUCTION TO THE STUDY OF FLUORINE, CHLORINE, BROMINE, AND IODINE.

On consulting the table it will be seen that the only other element which falls in this group is manganese; and that element we have, for good reasons, studied in another connection. The group is a very clean-cut and well-marked one. It shows, however, the same features we have encountered in other groups. Fluorine in some respects stands alone. For example, it forms *absolutely no oxygen compounds.* Chlorine, bromine, and iodine do form oxygen compounds. Again, fluorine compounds do not occur in nature associated with chlorine and the rest.

We have many times noticed how the leading element of a group imitates in some way the behavior of adjacent groups, particularly the leader of that group. There is no more striking instance than the way in which fluorine imitates oxygen. How this appears will be seen when we come to study the element more closely. Since fluorine shows so much individuality in its behavior, we will not consider it in connection with the other three, but will reserve it to be studied by itself.

Chlorine, bromine, and iodine constitute a very perfectly organized family of closely related elements. Some of the ordinary points are brought out by the following table:

Elements.	At. Wt.	State.	Color.
Chlorine..........	35.5	Gas	Greenish yellow
Bromine..........	80.	Liquid	Dark Red
Iodine............	127.	Solid	Gray, glittering, solid

We have to study, first, the elements themselves; second, their hydrogen compounds, and third, one or two of their oxygen compounds.

The most important compounds they form are their hydrogen compounds, which we have already met in other connections. These compounds are colorless gases, having the formulæ HCl, HBr, and HI, called hydrogen chloride, hydrogen bromide, and hydrogen iodide, respectively. Their water solutions react strongly acid and are called hydrochloric acid, hydrobromic acid, and hydriodic acid, respectively. The pure dry gases have no action upon litmus, and when liquefied, as they all can be by application of pressure and cold, the liquefied gases are not acids and do not act upon metals. The dissociation theory seems to point out a reason for this, for it asserts that the "acid" characteristics are due to the presence of hydrogen ions; and since the substances above mentioned do not conduct electricity at all when pure and free from water, it follows that they contain no free ions. The salts of the three acids are called chlorides, bromides, and iodides.

We have already seen how abundant sodic chloride is in nature, and it is not strange that it should be the main source of chlorine and its compounds.

The bromides and iodides are far less abundant. The salt-beds of Stassfurt are the most important source of the bromides from which bromine is manufactured. The chief source of iodine was sea-weed, until compounds of it were found as impurities in Chili saltpetre (sodic nitrate). Most of the iodine of commerce is now obtained from this source, though considerable is still made from deep-sea-weed which is washed ashore on the north and west coasts of France, Ireland, and Scotland. The sea-weeds are collected, dried, and carefully charred at as low a temperature as practicable (to avoid loss of iodine by volatilization). The iodine is then extracted by reactions, which will be better understood after a little laboratory work.

LABORATORY WORK.

All work in which there is evolution of chlorine, bromine, or iodine should be performed in a well ventilated room or under a good hood.

Avoid so far as possible inhaling the vapors of any of these substances. If any is inhaled accidentally, the quickest relief is found in inhaling the vapor of alcohol.

You will need for your work a few small crystals of potassic (or sodic) chloride, potassic bromide, and potassic iodide, besides a little manganese dioxide.

You will also need a test-tubeful of a solution of chlorine in water (chlorine water) and another of solution of bromine in water (bromine water).

Try to dissolve a very small fragment of iodine (about the size of a match-head) in water (about 10 c.c.). Shake the two together first without heating; afterward warm the water gently and shake. Does the iodine appear to go into solution? Try now its solubility in alcohol, chloroform, and carbonic disulphide. Pour off about two thirds of the water in which the fragment of iodine has been boiled into another test-tube; cool, and add one large drop of carbonic disulphide. Shake. The color of the drop of carbonic disulphide is due to iodine, which it has absorbed from the water.

Take half a test-tubeful of water and add to it about two drops of bromine water. Mix; then add a single drop of carbonic disulphide and shake. What happens.

These two experiments bring out beautifully the manner in which a substance behaves when confronted by two solvents at once, in both of which it dissolves, *the two solvents not mixing with each other.* Under these circumstances the substance distributes itself between the two solvents, and if the mixture be shaken for some time this distribution finally ends in two solutions of definite concentrations* in contact with each other. No amount of shaking can now change the state of things so long as temperature and quantities do not vary.

If the substance is very much more soluble in one of the solvents than it is in the other, as it is in both the present cases, most of the substance will be found dissolved in the liquid in which it is most easily soluble, and the practical effect is that a drop or so of carbonic disulphide seems to *extract*, or remove, from the water the little iodine or bromine it contains in solution. Keep in mind, however, that this is not, strictly speaking, the case, for there is *always* a distribution between the two solvents. This process of "extraction," or "shaking out" as it is sometimes called, is of frequent use. In the present case it is particularly useful, because the solution of iodine in carbonic disulphide or in chloroform has a beautiful rose-color; and this enables us to detect a very small amount of *free* iodine in water solution. The same is true of bromine, only the color of bromine in water solution is practically the same as that in carbonic disulphide or chloroform. Keeping in mind now that we can tell whether a solution contains *free* bromine or iodine, try the following experiments:

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* By this word *concentration* is meant the weight of dissolved substance per liter of the solvent.

1. To a few cubic centimeters of potassic iodide solution add, by means of a pipette, a *very small* drop of chlorine water. Shake, and note effect, if any. Add now a large drop of chloroform or carbonic disulphide, and shake thoroughly. What does the result show?

2. Repeat the experiment in the same way exactly, only add a small drop of bromine water instead of chlorine water. What is the result?

3. Take a little potassic bromide solution and add to it a very small drop of chlorine water. Add chloroform or carbonic disulphide as before, and shake. What is the result?

4. Set aside solutions of potassic chloride, potassic bromide and potassic iodide to crystallize. Compare the crystals as to form.

Ascertain, in a general way, which is the most and which the least soluble in water. How could you manage to conduct experiment 4 so as to answer this question?

ANOTHER METHOD OF LIBERATING THESE SUBSTANCES FROM THEIR COMPOUNDS.

1. Mix about 0.2 of a gram of potassic iodide with its own bulk of manganese dioxide. Place the mixture in a *dry* test-tube (keep the inner walls of the test-tube clean) and add about two drops

of concentrated sulphuric acid. (The acid should not be allowed to flow down the side of the test-tube, but should be dropped directly upon the mixture.) Heat gently. Note the color of the vapor that appears. What collects on the inner walls of the test-tube? Examine it with a lens. Scrape off a little and dissolve it in chloroform. What does it appear to be?

2. Try the same experiment with about 0.2 of a gram of potassic bromide. Pour a little water into the test-tube; shake and filter. Add to a portion of the solution a drop of chloroform and shake. Add a few drops of the remainder to a solution of potassic iodide. Shake out with chloroform.

The above liberation processes carried out on the large scale constitute the basis of the methods by which bromine and iodine are extracted. In case of chlorine, however, it is more convenient to act upon manganese dioxide with strong hydrochloric acid, as was described in connection with manganese.

CHLORINE, BROMINE, AND IODINE AS OXIDIZERS.

1. Warm a solution of ferrous sulphate containing some free sulphuric acid; add bromine water drop by drop until no ferrous test can be obtained.

2. Make a small quantity of manganous sulphate solution alkaline with sodic hydroxide. What is the precipitate? Write the reaction. Now heat it nearly to boiling and add bromine water. (If chlorine is available, pass some through another portion of the solution.) The precipitate in either case is $MnO(OH)_2$, in which the valence of manganese has been raised to four (see Manganese).

3. Warm a little powdered sulphur with strong bromine water for some time, then boil off the extra bromine (hood) and test the solution for sulphuric acid.

ACTION OF CHLORINE AND BROMINE UPON ORGANIC COLORING MATTERS IN PRESENCE OF WATER. BLEACHING.

Immerse strips of colored cloth in chlorine water and in bromine water for some minutes and note the effect.

Nature of this Oxidizing Action.—To half a test-tubeful of strong chlorine water add a freshly prepared solution of sodic sulphite, a drop at a time, with shaking, until the color of the chlorine is gone. Pass some more chlorine into the solution, then add more sodic sulphite as before. Do the same once more. Evaporate the solution somewhat to concentrate it, and test for the presence of sulphuric and hydrochloric acids.

Now, putting together the facts observed, whence does the oxygen seem to come in these oxidizing actions? What becomes of the chlorine or bromine?

The preparation of hydrochloric acid by the action of concentrated sulphuric acid upon sodic chloride is familiar. Hydrobromic acid may be made by acting upon potassic bromide (which is selected because it happens to be the most abundant of the bromides) by the action of sulphuric acid, only the acid must not be too strong or the resulting hydrobromic acid will be decomposed, as will be explained presently.' Prepare a little as follows: Add 14 grams concentrated sulphuric acid to 2 grams water (contained in a small beaker) with stirring, and cool the mixture. Now dissolve 12 grams potassic bromide in the smallest possible amount of hot water (beaker). While the solution is still hot, add slowly the whole of the sulphuric acid, stirring during the addition. Cool the solution thoroughly (by snow or ice if possible) and stir occasionally until the potassic sulphate has crystallized out; it is so sparingly soluble in water that only a very little will remain in solution. On filtering the solution through glass-wool or clean white sand a solution of hydrobromic acid will be obtained.

The Halogen Salts of Silver.—Prepare argentic chloride, argentic bromide, and argentic iodide by precipitation. Expose a little of each to sunlight for a while and note results. Note carefully the colors of the freshly precipitated substances. Try adding excess of strong ammonia to each of them. Warm gently. Note effects.

Next make a solution containing sodic chloride and potassic iodide (or any mixture of a chloride and an iodide). Add to it a single drop of argentic nitrate. What is the color of the precipitate? Try the effect of sunlight upon it. Does strong ammonia dissolve it? What does the precipitate appear to be?

Try the same with a mixture of a bromide and a chloride.

LECTURE 58.

CHLORINE, BROMINE, AND IODINE.

As brought out in the laboratory work, these elements are extracted from chlorides, bromides, and iodides by heating them with manganese dioxide and strong sulphuric acid. These processes are worth looking at for a moment, for according to the best of our present knowledge and belief the final result reached is, in each case, brought about through the agency of at least three reactions.

1. When concentrated sulphuric acid is warmed with manganese dioxide, oxygen is evolved and manganous sulphate is formed; thus,

$$MnO_2 + H_2SO_4 = MnSO_4 + O + H_2O.$$

2. When potassic bromide and sulphuric acid meet, we have seen that hydrobromic acid results:

$$2KBr + H_2SO_4 = K_2SO_4 + 2HBr.$$

3. Finally, when hydrobromic acid and just liberated (atomic) oxygen meet, the hydrogen of the acid unites with the oxygen to form water, and bromine is liberated; thus,

$$2HBr + O = H_2O + Br_2.$$

If we combine into one reaction the three given above, we have

$$2KBr + MnO_2 + 2H_2SO_4 = MnSO_4 + K_2SO_4 + Br_2 + 2H_2O.$$

Analogous reactions take place in case of chlorine and iodine, although in case of iodine there are some complications. The main reaction to notice carefully is the third one, where the acid is oxidized, for it is interesting from many points of view, and will merit more than a passing notice. We shall soon meet it in our study of the individual elements.

CHLORINE

is a yellowish-green gas, about 2.5 times as heavy as air, somewhat soluble in water and decidedly active chemically. It unites directly with most of the metals, even at ordinary temperatures. Some metals (e.g., powdered antimony or thin copper leaf) take fire when thrown into it.

When a long tube filled with a water solution of chlorine (which is yellowish-green like the gas) is inverted in a dish of the same solution and allowed to stand in bright sunlight, it slowly loses its color. The solution turns acid, and a bubble of gas collects at the top of the tube. This gas turns out to be *oxygen*, and the acid in solution is easily shown to be *hydrochloric acid.* Since only chlorine and water were present in the tube, it is easy to see that the oxygen has been liberated from water by the chlorine which has united with its hydrogen, perhaps thus:

$$H_2O + Cl_2 = 2HCl + O.$$

At least this is the reaction proper. Under the conditions given above, of course, the oxygen atoms unite at once to form the oxygen molecule. For our present purposes, however, let us take the reaction just as it stands.

Recall now the reaction we were considering a few moments ago—that in which hydrobromic or hydrochloric acid is oxidized by atomic oxygen—and it will be seen that *the one we have before us is the direct reverse of it.* The fact, then, seems to be that we are dealing with another marked case of an easily reversible reaction,

$$H_2O + Cl_2 \rightleftarrows 2HCl + O,$$

and the direction in which the reaction runs depends upon the conditions. If there is a constant supply of atomic oxygen in the field (as in the action between potassic chloride, manganese dioxide, and sulphuric acid), the reaction runs "from right to left"—that is, most of the hydrochloric acid ultimately gets oxidized. But if there is no such constant supply of oxygen, and *if there is some substance present in the field which is acted upon by oxygen,* the reaction runs "from left to right," and the chlorine is all ultimately converted into hydrochloric acid. A solution of chlorine in water changes only very slowly if kept in the dark; in the light it changes fairly rapidly, the sunlight furnishing, in some unexplained way, the necessary energy to carry the reaction through completely in spite of the efforts of the oxygen to run it back again.

We can now understand why chlorine acts as an oxidizer in presence of water. Bromine and iodine act in the same way, only less powerfully. Some of these oxidation reactions are easily understood. For example, the oxidation of freshly precipitated manganous hydroxide to manganous acid ($MnO(OH)_2$) takes place thus:

$$Mn(OH)_2 + Cl_2 + H_2O = MnO(OH)_2 + 2HCl.^*$$

The oxidation of sulphur by bromine water:

$$S + 2Br_2 + 2H_2O = SO_2 + 4HBr.^*$$

Some reactions, however, are not so easily explained. For example, when an acid solution of ferrous sulphate is changed to ferric sulphate by some oxidizing agent, like bromine, what part does the oxygen play? When the reaction is over we have simply a sulphate of iron containing a larger proportion of SO_4 than before—i.e., we have passed from $FeSO_4$ to $Fe_2(SO_4)_3$. In what sense is it proper to call this oxidation? As a matter of fact most of the reactions by which we raise the valence of an element involve oxidizing agents. Ferrous sulphate cannot be changed to ferric sulphate by adding more sulphuric acid, nor can ferrous chloride be changed to ferric chloride simply by adding more hydrochloric acid; but if only atomic oxygen be present, the metal seems suddenly to acquire the power to take on more of the acid ion, or, in other words, its valence changes. These facts are probably connected with the very general fact that the elements as a whole show a greater uniting power or valence toward oxygen than they do toward any other element, and it may be that the oxygen simply tempts the metal to offer its extra bonds, so to speak. To show what is meant here in a very rough way, take the case of ferrous sulphate. Suppose an oxygen atom approaches; the ferrous sulphate, perhaps, behaves thus,

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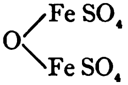
* Analyze these reactions.



forming a sort of basic *ferric* sulphate, which is instantly acted; upon by the sulphuric acid; thus,

$$Fe_2(SO_4)_2O + H_2SO_4 = Fe_2(SO_4)_3 + H_2O.$$

It is of course very difficult to bring positive proof that this is really what takes place, but the explanation is a fairly simple one, and all the facts available are in accord with it. In order to show how it applies, two such reactions will be given in full:

$$2FeSO_4 + H_2SO_4 + Br_2 + H_2O = Fe_2(SO_4)_3 + 2HBr + H_2O;$$
$$2FeCl_2 + Cl_2 + 2H_2O = 2FeCl_3 + 2H_2O.$$

The two foregoing reactions are usually found written thus:

$$2FeSO_4 + H_2SO_4 + Br_2 = Fe_2(SO_4)_3 + 2HBr;$$

$$2FeCl_2 + Cl_2 = 2FeCl_3;$$

and there is no objection to their being so written, provided it be understood that they are simply abbreviated forms of the actual reactions and leave out some of the reacting substances and some of the products.

This oxidizing action of chlorine and bromine is the principal cause of their bleaching action. Many artificial and natural dyestuffs are converted by oxidation into colorless compounds, and when such colors come in contact with *moist* chlorine they are bleached *by the oxygen*, not by the chlorine. Some colored compounds unite directly with chlorine, forming colorless compounds, and sometimes the bleaching is due to this cause.

Hydrogen chloride is a colorless, heavy, pungent-smelling gas, exceedingly soluble in water. Its tendency to dissolve in water is so great that when it escapes into the air it seizes upon the moisture of the air and dissolves in it. Since the solution has necessarily a lower vapor pressure than water, it condenses, and we see white mist appear wherever the gas goes; or, as the common expression is, the acid "fumes" in the air. The more moist the air, the more it fumes.

When hydrogen and chlorine are mixed in equal volumes and exposed to bright sunlight, the mixture generally explodes, the union of the two gases taking place with great rapidity. In the dark no perceptible action takes place. Hydrogen burns in chlorine and chlorine burns in hydrogen, the product in each case being hydrogen chloride. The water solution of the gas is *hydrochloric acid*, and the strong acid of the laboratory contains about 37% of hydrogen chloride. Like the other acids we have met with, it loses in strength when boiled, and grows weaker until it contains about 20% acid, when it distils over unchanged. If we start with a very weak solution it grows stronger on boiling, only water going off, until it reaches the same point as before, i.e., contains about 20% "real acid," when it distils over unchanged. The dissociation theory explains this by the almost complete dissociation of very dilute hydrochloric acid. Hydrogen and chlorine ions cannot leave the solution as such, and so at first all that goes is water, but as the solution grows stronger the dissociation decreases, and when a certain percentage of undissociated molecules have formed, hydrochloric acid becomes perceptible in the liquid, which distils over. When hydrochloric acid of any strength is boiled, at least two opposing tendencies are at work at the surface of the liquid—the tendency of the gas to dissolve, and the tendency to be driven out from the solution at the temperature prevailing. If we boil a strong hydrochloric acid more gas is expelled in a given time than is dissolved, and as a result the solution weakens. Finally, however, it comes to the inevitable state of equilibrium, and we then begin to get a mixture of acid and water in constant proportions, which, however, vary as the barometer pressure varies.

BROMINE

is a very dark-red liquid, over three times as heavy as water, and having a very pungent, irritating odor. It attacks the skin, forming sores which are like severe burns. It is extensively used in laboratories and in some manufacturing processes. It boils at 59°. It oxidizes and bleaches as chlorine does, only less powerfully.

Hydrogen bromide is, like hydrogen chloride, a colorless, pungent gas, very soluble in water. The solution is much like that of hydrochloric acid in its general behavior. It may be prepared:

(1) By passing a mixture of hydrogen and bromine vapor

through a heated glass tube and absorbing the gaseous product in water.

(2) By the action of potassic bromide upon sulphuric acid. If the strongest sulphuric acid be used, the hydrogen bromide *reduces* the sulphuric acid, forming sulphurous acid, thus:

$$H_2SO_4 + 2HBr = H_2SO_3 + H_2O + Br_2 .$$

If the solution be warm, *part of* the bromine goes off as vapor; some stays in solution.

There are other methods, but they need not be considered here.

IODINE

is a grayish-black crystalline solid, slightly volatile at ordinary temperatures, sparingly soluble in water; easily soluble in alcohol, chloroform, or carbonic disulphide. It attacks the skin, uniting with the tissues to form brown compounds. It has some usefulness in reducing swellings, to which it is usually applied in the form of an alcohol solution, called by the druggists *tincture of iodine.* It acts as an oxidizer in presence of water, but rather feebly in most cases.

Hydrogen iodide cannot be conveniently made by the methods used in the other cases. It is usually made by bringing together red phosphorus, iodine, and water. First phosphorus triiodide is formed thus:

$$P + I_3 = PI_3 ,$$

then

$$PI_3 + 3H_2O = P(OH)_3 + 3HI.$$

It decomposes, when moderately heated, into hydrogen and iodine. Its water solution is hydriodic acid. In presence of easily oxidized substances it gives up hydrogen and liberates iodine, and is, accordingly, a good reducing agent.

OXYGEN COMPOUNDS OF CHLORINE, BROMINE, AND IODINE.

Chlorine forms at least three oxides and four acids containing oxygen.

Bromine forms no oxides, but forms two oxygen acids.

Iodine forms one oxide and two oxygen acids.

Of these compounds only one or two will be considered.

Hypochlorous Acid, $HClO$.—This acid is worth mentioning, because its calcium salt, $Ca(ClO)_2$, is probably one of the constituents of "bleaching powder," or "chloride of lime," which is made by passing chlorine over slaked lime. When it is to be used for bleaching, the powder is treated with water and dilute acids, when there is obtained, on filtering, what amounts to a very strong chlorine water.

Chloric Acid, $HClO_3$.—The most common salt of this acid is *potassic chlorate*, which is made by passing chlorine into a strong solution of potassic hydroxide. A mixture of potassic chloride and chlorate is formed, and as the chlorate is less soluble in water than the chloride, it crystallizes out first when the solution is concentrated. *It is a powerful oxidizer, and should never be ground or roughly mixed with easily oxidizable substances. Neither should it ever be allowed to come in contact with concentrated sulphuric acid, for an oxide of chlorine is liberated which is dangerously explosive.*

When potassic chlorate or in fact any chlorate, is heated, oxygen is given off, and the chloride remains behind. Potassic chlorate is extensively used in the preparation of oxygen. It is generally mixed with manganese dioxide, as under these circumstances the gas comes off at a much lower temperature than when the salt alone is heated. A number of other substances serve the same purpose. Most of them are metallic oxides, and this fact has suggested that perhaps the oxide acts by attracting the oxygen from the chlorate to form a higher oxide, or at least some more highly oxidized compound, which in turn breaks down as fast as formed, liberating oxygen. This explanation seems to have some facts in its favor in case of such oxides as manganese dioxide, but it does not explain why such substances as kaolin and finely divided platinum have the same effect. The full explanation is evidently not yet found.

Relations between Chlorine, Bromine, and Iodine.—Our laboratory work has shown that free bromine will expel iodine from iodides, and that chlorine will expel either bromine or iodine from the chlorides or iodides. The reactions are

$$2KI + Br_2 = 2KBr + I_2.$$
$$2KBr + Cl_2 = 2KCl + Br_2.$$
$$2KI + Cl_2 = 2KCl + I_2.$$

Moreover, the three compounds, HCl, HBr, and HI, show very different degrees of stability. It requires a temperature of about 1600° to split hydrogen chloride into its elements to any appreciable extent. Hydrogen bromide begins to decompose at 800° and hydrogen iodide at 180°.

At first glance these relations seem to be very simple and to point to stronger "affinities" for metal or hydrogen as we pass from iodine to chlorine. A little reflection, however, shows that the simple-looking reactions given above take place in water solution, and hence must be influenced by many matters, such as solubility, dissociation, etc. Indeed, one can almost see a reason for the first reaction without invoking affinities at all. Potassic chloride is much less soluble in water than potassic iodide; and iodine is enormously less soluble than bromine. All our studies thus far would lead us to predict a very decided reaction in the direction of these more insoluble products; and these remarks apply with increased force to the third reaction, for here the difference in solubilities is still greater.

Moreover these reactions are, to some extent, reversible. When metallic chlorides are moderately heated with bromine vapor in sealed tubes more or less chlorine is replaced by bromine, and we reach ultimately a state of equilibrium between the metallic chloride, chlorine, the metallic bromide and bromine; and the relative quantities of these four substances depend largely upon the quantity of bromine added in the first place.

Again, when excess of a concentrated solution of potassic bromide is poured over argentic chloride and allowed to stand, all the argentic chloride is converted into bromide, according to the reaction

$$AgCl + KBr = AgBr + KCl.$$

Similarly potassic iodide converts argentic chloride into iodide; thus,

$$AgCl + KI = AgI + KCl.$$

Here the controlling fact is that the insolubility of the silver salts increases as we pass from the chloride to the iodide.

Enough has been said to show that these reactions, like all others we have studied, take different courses, and produce different results according to circumstances. It is not enough to know what the reacting substances are. We must know the circumstances under which they are to react, their solubilities, degree of dissociation, the concentration of the solutions, etc., and we must possess the same knowledge concerning the products of the reaction. *In cases where we possess all this knowledge it is possible to predict what will happen not only qualitatively but quantitatively.*

When we wish to test a solution for the presence of an iodide we add a drop of chlorine water or of bromine water, and then test for free iodine in the solution. This can be done by "shaking out" as has been described, or by adding a little starch paste, which forms a characteristic purplish-blue compound with iodine.

To test for a bromide we add a drop or two of chlorine water and then test for free bromine. The best way to do this is to dip into the liquid a fragment of filter-paper which has been soaked in starch paste containing potassic iodide. If bromine is present it liberates iodine from the potassic iodide and thus colors the starch blue.

If all three—a chloride, a bromide, and an iodide—are present in the same solution we first make the tests above described. If both iodine and bromine are found we proceed to get them out of the way, so that we can test for chlorine. To do this we boil the solution with dilute sulphuric acid and a crystal of potassic permanganate, which drives off the bromine and the iodine. The boiling is continued until a strip of iodized starch paper held in the steam is not colored blue. The excess of permanganate is then decomposed by warming with a little alcohol. The solution is filtered and the chlorine tested for with argentic nitrate.

FLUORINE,

as has been remarked, stands by itself among all known elements in some respects. It is the most active of all the elements when in the free state, and unites readily with practically all the other elements *except oxygen, platinum, and nitrogen.* The element itself is obtained by electrolizing hydrofluoric acid (HF) in a platinum decomposing-cell. It is a gas with a faint greenish-yellow tint. It rapidly decomposes water, forming hydrofluoric acid. The oxygen liberated always contains considerable ozone.

Hydrofluoric Acid and its Salts.—The acid is obtained when the metallic fluorides are heated with concentrated sulphuric acid. It is a colorless fuming liquid which acts powerfully upon the skin and upon the membranes of the throat, nose, and eyes. It is a dangerous substance to handle. It is in some ways like hydrochloric acid, but it has one feature in which it stands absolutely alone among the acids. *It dissolves glass, sand, and silicates generally.* This dissolving action depends upon the fact that hydrofluoric acid acts upon silicic oxide (SiO_2) just as it would act upon a basic oxide, forming a gaseous fluoride of silicon, SiF_4; thus,

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

This fact makes it necessary to keep the acid in bottles made either of rubber or of paraffin. It also makes it impracticable to work with it except in dishes of platinum; but the acid is of very great use in *etching* the graduation lines on barometer and thermometer tubes. The tubes are first covered with a layer of wax and the marks scratched through the wax. Then the tube is exposed to the vapors of hydrofluoric acid, which etches wherever the wax has been scratched through.

The salts of hydrofluoric acid are called *fluorides.* They are fairly abundant in some localities, particularly *fluorite* or *fluorspar*, which is calcic fluoride,—and *cryolite*, which is, as we have seen, a double fluoride of aluminum and sodium (Na_3AlF_6). These substances are both nearly insoluble in water. The fluorides are as a rule less soluble in water than the corresponding chlorides and bromides.

The most curious thing, though, about fluorine is the way in which it imitates oxygen. The most noteworthy piece of imitation consists in forming acids just like the oxygen acids, only with two fluorine atoms in the place of each oxygen atom. For example, when silicon fluoride is brought into hydrofluoric acid in the proportions of two molecules of hydrofluoric acid to one molecule of silicon fluoride a new acid is formed, which has the formula H_2SiF_6 and is called fluosilicic acid. It forms quite stable salts called fluosilicates. The potassium or sodium salts are very easily obtained by simply neutralizing the acid with sodic or potassic hydroxide.

These salts are close imitations of the silicates, though they are as a rule not so insoluble. Their formulæ have the curious relationship mentioned above, each oxygen atom of the silicate being replaced by two fluorine atoms in the fluosilicate. Moreover fluorine succeeds in carrying out the same programme with many of the metallic elements with which it unites, especially when that metal happens to have any acid-forming tendencies. Cryolite is a good example. This is an attempt on the part of fluorine to imitate sodic aluminate ($Na_2\,Al\,O_3$); the result being Na_3AlF_6, in which each oxygen atom is replaced by two fluorine atoms.

INTRODUCTION TO THE STUDY OF CARBON, SILICON, TIN, AND LEAD.

THIS group, like several of the preceding ones, is best subdivided. Tin and lead are quite distinct from silicon and carbon in appearance, physical properties, and some of their chemical behavior. On the other hand, the group presents, on the whole, quite a strong set of analogies throughout; but these are confined to those compounds in which tin and lead are at their highest valence (four), under which circumstances they show decided acid-forming tendencies; and the acids they form are analogous to carbonic acid.

It will be best to study tin and lead first, then silicon, and finally carbon.

LABORATORY WORK.

TIN.

Try the action of strong and dilute acids on small fragments; heat gently in each case. *Do not forget to be very careful in using strong sulphuric acid.* In which cases do you get clear solutions? Are there any cases in which there is no action? What do you obtain in case of strong nitric acid? Have you any reason to doubt that the product is a nitrate? Do you recall any case in which nitric acid acting upon an element did not produce a nitrate? (See p. 291, Exp. 2, and look in your note-book for the results.) What is the result with dilute nitric acid? How do the alkalies NaOH and KOH act upon tin?

Two Sets of Tin Salts.—Dissolve a few small fragments of tin in the least possible amount of hot hydrochloric acid. Dilute the solution with its own volume of water. To half of this solution add H_2S and note the color of the sulphide which precipitates. Heat the other half and add to it bromine-water drop by drop as long as it is decolorized. Then add to a portion of the solution H_2S. Note the color of the sulphide. What becomes of the bromine in the above process? Name some other substances which could have been used as oxidizing agents in this case. In which of these solutions you have prepared is the valence of tin the higher? How can you convert this solution back into the lower form again? Try it.

The Lower Chloride of Tin (Stannous Chloride) and its Use as a Reducing Agent.—This salt is selected because it is about the only common and moderately stable salt of tin. The other stannous salts would, of course, show the same power.

Dissolve a few crystals of the chloride in water. Is the solution clear? Test with litmus. Do you recall any cases similar to this? Add a little strong hydrochloric acid (a few drops only). Try now the action of this solution (or portions of it) on solutions of potassic dichromate, ferric sulphate (both solutions should be slightly acid), and mercuric chloride. What is the precipitate in this latter case? Filter it off. Wash it with water. Dissolve in a little nitric acid, dilute; divide the solution and test for mercury (see pp. 345–346) and for chlorine. What reaction probably takes place when stannous chloride and mercuric chloride are mixed in water solution?

Behavior of the Hydroxides of Tin toward Alkalies.—To a clear solution of stannous chloride add sodic hydroxide drop by drop as long as precipitate falls; then add at once an excess of the reagent. What takes place? Cite some similar cases. Oxidize a solution of stannous chloride to stannic chloride; then add sodic hydroxide in the same way as before. Can you suggest any explanation of these observations?

LEAD.

Try the action of acids in the same way as in the case of tin. Try also the effect of water on lead-filings. Leave the filings standing for some days in contact with water; then concentrate the solution and test for lead by adding dilute sulphuric acid, in which case white plumbic sulphate is formed, or add hydrogen sulphide, in which case black plumbic sulphide is formed if lead is present.

Try the action of litmus upon solutions of plumbic nitrate and plumbic acetate.

Precipitation of Metallic Lead by Zinc.—Make a clear solution of plumbic acetate in water, suspend in it a strip of zinc, and allow it to stand for several hours. What becomes of the zinc, and what appears in its place?

Prepare the carbonate, hydroxide (try the effect here of excess of alkali as in case of tin), chromate, sulphide, chloride, bromide, and iodide of lead (all sparingly soluble salts). Of the last three which is the most insoluble? Write the reactions involved in the above preparations.

Oxides of Lead.—Heat a small piece of metallic lead to as high a temperature as possible on a piece of asbestos paper, stirring occasionally to expose fresh surfaces. Note the color and appearance of the product. Mix some of it with twice its bulk of lampblack or powdered charcoal and heat as hot as possible in a piece of hard-glass tubing sealed at one end. Cool the tube, shake the contents out and examine with a lens. Heat to redness a small crystal of plumbic nitrate on a piece of asbestos paper, and see if the product is like that obtained by the previous process. What do metallic nitrates become, as a rule, when heated?

Another Oxide of Lead.—Place a gram or so of the yellow oxide in a test-tube and boil it with dilute nitric acid. Note changes. Try another method of making it. Place some of the yellow oxide in a test-tube, add sodic hydroxide and bromine water; or, if convenient, pass chlorine through the mixture; heat nearly to boiling. Try still another method. Place a very little of the yellow oxide in a test-tube with sodic hydroxide solution and add a few drops of hydrogen dioxide solution. Heat nearly to boiling. From the nature of these methods of preparation, what seems to be the relation between these two oxides?

Try heating some of the oxide you have just prepared (which will be furnished you) in your little hard-glass tube. What changes take place? Is anything given off? What is it? Try heating a little with concentrated hydrochloric acid in a test-tube. Very carefully note the odor of the gas that comes off. Also try its action upon a moist piece of colored cloth. What does it appear to be? Heat a little of the oxide (gently) with concentrated sulphuric acid. What comes off?

Finally, heat some strong potassic hydroxide solution to boiling in a test-tube. Add slowly the brown oxide of lead little by little. What becomes of it? What kind of an oxide does this appear to be?

LECTURE 59.

TIN AND LEAD.

TIN and lead occur quite abundantly in nature, but not in the free state. The most common compound of lead, and its most valuable ore, is the sulphide PbS, which is called *galena* or *galenite*. The most important ore of tin is its highest oxide, SnO_2, which is found at Cornwall, England, and in some localities in this country, though not very abundantly.

Lead forms a greater variety of compounds than does tin. There are certainly five oxides:

Pb_2O,	Plumbous oxide (black), very feebly basic	N_2O	——
PbO,	Plumbic oxide (yellow), basic	NO	MnO
Pb_3O_4,	Triplumbic tetroxide (red) (no distinct characteristics)	——	Mn_3O_4
Pb_2O_3,	Plumbic trioxide (yellow-red) (no distinct characteristics)	N_2O_3	Mn_2O_3
PbO_2,	Plumbic peroxide (brown) feebly acid and feebly basic.	NO_2	MnO_2

For convenience of comparison the corresponding oxides of nitrogen and manganese are put opposite, so that it can be seen how closely lead imitates both nitrogen and manganese in the formulæ of the oxides.

In the matter of behavior the analogies between the oxides of lead and the corresponding ones of manganese are very striking. In so far as we have time to study these oxides we will keep these analogies in mind.

Tin forms only two oxides:

SnO,	Stannous oxide	(black).
SnO_2,	Stannic "	In nature as black crystals (the artificial oxide is white).

In its behavior it resembles the members of its own group and has not many outside analogies. Its higher oxide is an acid-forming oxide, but it forms some salts, and these are not excessively unstable. They will not stand boiling with water, however. All of them decompose under this treatment and give stannic hydroxide and the acid.

We will now consider lead and its compounds.

The metal is obtained mostly from *galena* by processes which are substantially as follows:

The ore is first roasted in a current of hot air. This acts in two ways—shown by these reactions:

$$1.\ 2PbS + 3O_2 = 2PbO + 2SO_2.$$
$$2.\ PbS + 2O_2 = PbSO_4.$$

The time of heating, quantity of air, etc., are so regulated as to produce after a certain time a mixture of oxide, sulphate, and unaltered sulphide. The doors of the furnace are then closed and the mixture is heated without admitting any more air, when these reactions take place:

$$PbS + 2PbO = 3Pb + SO_2;$$
$$PbSO_4 + PbS = 2Pb + 2SO_2.$$

Sometimes another process is employed. The ore is simply heated with metallic iron, which removes the sulphur, forming ferrous sulphide and metallic lead.

$$PbS + Fe = FeS + Pb.$$

The metal as prepared by either of these processes, or in fact as obtained from any of its ores, always contains traces of silver, and processes have been devised by which this very small amount of silver can be profitably extracted.

The first step is always to "concentrate" the silver, and two processes will be described by which this can be done. Both of them are exceedingly interesting applications of principles.

1. When lead containing a little silver is melted we have virtually a solution of silver in lead, comparable with a solution of salt or sugar in water. Now when a dilute salt solution is cooled down to its freezing-point it will be remembered that what separates is ice, or, in general, where a dilute solution in any solvent is cooled so as to freeze gradually, it is the pure solid solvent which separates first. When this solution of silver in molten lead is cooled slowly and carefully, it soon reaches its "freezing-point," and here, as in other cases, the pure solvent separates first. As the lead crystals form, they sink to the bottom of the pot and are ladled out with a long-handled perforated ladle. It is not worth while to follow out the details, especially as the process is now out of date, but it can be seen how the silver is by this means obtained finally in a much more concentrated solution than at first. This is called the Pattinson process.

2. The second process depends upon a different principle. The lead is melted down and a small quantity of zinc is added. Zinc does not dissolve in lead very readily, but dissolves silver more easily than does lead. The result is that it behaves exactly as a drop of carbonic disulphide or chloroform does in a water solution of free bromine or iodine, i.e., it *extracts* the silver when stirred up with the lead-silver alloy, and being lighter than lead rises to the surface, forming a "scum" which contains practically the whole of the silver. This is called the Parkes process.

From the rich alloys of lead or zinc and silver resulting from these processes the silver can be obtained by oxidizing the lead or zinc. In the case of lead this is accomplished by heating in the air. In the case of zinc the oxidation is usually brought about by heating to a high temperature in a current of superheated steam.

Lead is a soft, easily melted metal, with a slight blue tinge, not very strong, but quite malleable. Its uses in the form of pipe, in constructing the sulphuric acid chambers, and in making shot are well known. It is slightly dissolved by *pure* water, and enough so to make it undesirable to have drinking-water brought in lead pipes. Hard waters (i.e., those containing in solution the carbonates and sulphates of calcium and magnesium) attack it at first, but the result is the formation of a coating of plumbic sulphate or carbonate on the metal, and this coating, being practically insoluble in water, prevents further action.

COMPOUNDS OF LEAD.

The only salts of importance are those corresponding to plumbic oxide (PbO). These salts are fairly stable. *Plumbic chromate*, a bright-yellow powder, sparingly soluble in water, is used as a paint under the name of *chrome yellow*.

Plumbic carbonate is interesting because a near relative of it is what we use as a paint under the name of *white lead*. When we undertake to make the carbonate by precipitation it is partially decomposed by the water, as the salts of rather weak metals usually are, with formation of a set of complex basic salts, i.e., salts in which part of the acid ion is replaced by hydroxyl. For instance, one of them has a composition roughly represented by the formula

$$2PbCO_3.Pb(OH)_2 \text{ or } Pb_3(CO_3)_2(OH)_2.$$

White lead is made by several methods, none of which will be described here. They all involve the same chemical changes, namely, the production of a basic lead acetate, starting with either metallic lead or the yellow oxide (PbO), and the conversion of this basic acetate into basic carbonate by carbonic dioxide. It is an excellent white, only it is turned brown or black by hydrogen sulphide, which forms the black plumbic sulphide.

Plumbic oxide is formed when lead is heated in the air. It is a yellowish powder. Its commercial name is *litharge*. It is used in making white lead; and it dissolves in the strong alkalies, forming salts like the zincates. These salts are called *plumbites*:

$$2NaOH + PbO = Na_2PbO_2 + H_2O.$$

The same result can be reached by dissolving the hydroxide in sodic hydroxide.

Triplumbic tetroxide, Pb_3O_4 (*minium*, or *red lead*), is made by carefully heating litharge in the air. It was formerly regarded as a mixture of PbO and Pb_2O_3, but it evidently is not, for it is not affected by acetic acid, while PbO is. It has no well-defined properties. It appears to be a definite compound, but its constitution is not certainly known. It is used mixed with oil to make the joints of gas and water-pipes tight. When heated to a fairly high temperature it gives oxygen and litharge (PbO).

Plumbic peroxide, PbO_2, is made by the action of oxidizing agents upon the lower oxides of lead, usually in presence of alkalies. We have already taken up these methods in the laboratory. Some of the reactions are simple; for example, when hydrogen peroxide is used,

$$PbO + H_2O_2 = H_2O + PbO_2.$$

When bromine is used,

$$PbO + Br_2 + H_2O + 2NaOH = PbO_2 + 2NaBr + 2H_2O.$$

The alkali is necessary to prevent the HBr from converting the oxide into plumbic bromide.

The oxide is a heavy brown powder which is insoluble in water, and which reminds one strongly of manganese dioxide.

It gives chlorine with strong hydrochloric acid, and oxygen with strong sulphuric acid, forming plumbic tetra-chloride in one case and sulphate in the other. It acts as an excellent oxidizing agent when boiled with either acids or alkalies.

Plumbic acetate is the substance known as *sugar of lead*—a violent poison. It is made by dissolving plumbic oxide in acetic acid and crystallizing out the salt.

TIN

is prepared by reducing the ore (SnO_2) with charcoal in a suitable furnace. The metal has to be refined by a process called *liquation*. It consists in heating the impure tin till it begins to melt, and then running off the metal as fast as it melts. The pure tin melts first, and by carefully regulating the temperature the impure part is left unmelted. It is a white metal, soft and easily worked under the hammer. It may be beaten out into very thin sheets (tin-foil). If melted, poured into an iron mortar and stirred vigorously with the pestle as it solidifies, considerable of it is reduced to a crystalline powder.

Melted with copper it forms various alloys known as *bronzes*. It is also used to coat the surface of sheet-iron for making cooking-utensils. The process is much like "galvanizing" (see Zinc).

Stannic oxide is formed when tin is heated to a high temperature in contact with air or oxygen. It is an acid-forming oxide, and when fused with sodic or potassic hydroxide reacts thus:

$$SnO_2 + 2NaOH = Na_2SnO_3 + H_2O.$$

Compare this reaction with the one where sodic carbonate is made by passing CO_2 into NaOH :

$$CO_2 + 2NaOH = Na_2CO_3 + H_2O.$$

The product is called sodic stannate and is used as a "mordant" in dyeing.

Stannic chloride is formed when tin is heated in a current of chlorine. It can be dissolved in cold water without much change, but hot water at once decomposes it, just as is usually the case with the chlorides of weakly basic metals. The complete decomposition would be

$$SnCl_4 + 4H_2O = 4HCl + Sn(OH)_4,$$

but in reality what we obtain is a substance having the formula

$$H_2SnO_3,$$

which is the hydroxide above given less one molecule of water. This substance, H_2SnO_3, is called stannic acid and is analogous in formula to carbonic acid, H_2CO_3.

The sulphides of tin have been prepared in the laboratory. There is one interesting thing about stannic sulphide, and that is that when it is treated with sodic, potassic, or ammonic sulphide it forms with the alkaline sulphide a *sulphostannate* of the alkali metal—that is, a salt just like sodic stannate, *only with sulphur in the place of oxygen*, thus:

Na_2SnO_3, sodic stannate.
Na_2SnS_3, sodic sulphostannate.

The sulphides of arsenic and antimony act similarly. We obtain by precisely the same method sulpharsenates, sulphantimoniates, sulpharsenites, and sulphantimonites, thus:

Na_3AsO_3, sodic arsenite,
Na_3AsS_3, sodic sulpharsenite,

and so on. The important thing is that these substances are *soluble in water*, and that means that if we had in solution a mixture of arsenic, antimony, and tin compounds, with the compounds of other metals, we could easily separate all the arsenic, antimony, and tin from the rest of the metals. For by treating the solution with H_2S the arsenic, antimony, and tin, together with the sulphides of some of the other metals present, would be precipitated as sulphides. Now by filtering off the sulphides and treating them with a warm solution of Na_2S or $(NH_4)_2S$, the sodic sulphostannate, sulpharsenate, etc., would be formed and pass into solution, the other sulphides remaining untouched. (See under Antimony.)

LECTURE 60.

SILICON AND CARBON.

We have seen that lead and tin both form at least two sets of compounds, and that lead forms compounds which show that its valence toward oxygen may be one, two, or four.

Silicon never shows but one valence (four) so far as we know. The valence of carbon is usually four. In carbonic oxide (CO) it is probably two.

Silicon forms a number of compounds, in most of which it appears as an acid-forming element, and the salts of the acids it forms—the silicic acids—are widely distributed and of great importance. The greater part of the earth's crust is made up of the silicates of different metals. It is distinctively *the* element of inanimate nature.

But notwithstanding the great prominence thus given to the silicon compounds, there is a great gap between it and carbon. In point of chemical behavior this latter element stands alone. Not only does it form compounds almost without number, but these compounds show peculiar features which seem to set them apart from all other compounds of which we have any knowledge at present. In nature they play a most interesting and important part, forming as they do the greater part of all living things, whether animal or vegetable. The compounds concerned here are for the most part very complex. From the fact that the carbon compounds present such peculiarities in their chemical behavior it was believed, for a long time, that they could not be formed without the intervention of a certain mysterious principle to which was given the name *vital force*, and which was supposed to be possessed by all forms of organized life. This view was dispelled by the actual preparation (by Wöhler in 1823) of *urea*, a substance which, up to that time, had been known only as one of the products of animal life-processes. To-day we know that it is *possible* to make any one of the compounds existing in animal or vegetable organisms in the laboratory, starting simply with the elements, though comparatively few have been made, owing to the great difficulty and complexity of the processes involved.

We do, however, find it convenient to study certain of the carbon compounds, namely, those in which it is united with hydrogen, or with hydrogen and nitrogen, or with hydrogen, nitrogen, and oxygen by themselves, mainly on account of the enormous number of them. The branch of chemistry dealing with these compounds is called *Organic Chemistry*. We can only take a glance at some of the simplest of these compounds.

Silicon never occurs free in nature. Carbon does, however, and in several different forms. *Graphite* and *diamond* are the purest forms of natural carbon. The various kinds of coal are more or less impure carbon. Charcoal, coke, lampblack or soot, and bone-black (animal charcoal) are artificial forms.

It will probably be best to begin our study in the laboratory, where we shall spend most of our time with carbon and its compounds, as there are very few things we can do with the silicon compounds.

LABORATORY WORK.

Place in a small piece of hard-glass tubing about two grams of white sugar, starch, paper, wood, or leather, whichever happens to be most convenient. All these are substances formed in either plant or animal life-processes and contain carbon, hydrogen, nitrogen, and oxygen.

Adapt a delivery-tube as usual; arrange a test-tube or small jar to collect gases over water if necessary. Mount the tube in position, with the delivery-tube dipping under water, and begin gently heating the hard-glass tube. Continue to heat as long as there is any change; then disconnect the tube and cool the whole. Has any gas collected? If so, find out as much as you can about its properties. Have you noticed any other products? What does the residue in the tube suggest by its appearance?

Heat a small portion of one of the substances above mentioned as hot as possible on a piece of platinum-foil, or, if this is not available, on a thin piece of asbestos paper. Use the full heat of your flame, and allow the heating to go on for some time. Describe what takes place as accurately as you can. Is the final result the same as in the previous case?

Carbonic Dioxide—Formed when Carbon Burns in the Open Air or in Oxygen.—1. Pour into a test-tube about 1 c.c. of hydrogen peroxide solution. Add a few drops only of sodic hydroxide.

Fix a piece of charcoal the size of a large pea in a loop in the end of a piece of copper wire about 6 inches long. Heat the charcoal in the flame till it is ignited. Now heat the solution in the test-tube gently, when oxygen will be given off. Lower the glowing charcoal into the test-tube, and let it burn there as long as it will. Carefully pour the gas into a test-tube containing lime-water. Shake.

2. Simply lower another such glowing coal into a small flask containing only air. When it goes out remove it, and pour a little lime-water into the flask. Shake.

3. Place in a test-tube about 2 c.c. of a strong solution of potassic dichromate. Add half as much concentrated sulphuric acid. This is one of the most powerful liquid oxidizing mixtures. Adapt to the test-tube a delivery-tube passing into the mouth of a second test-tube containing lime-water. *The delivery-tube must not touch the lime-water.* Drop into the oxidizing mixture a fragment of charcoal; replace the stopper, and heat the mixture gently until it boils. After a few moments'

heating take away the lime-water tube, close it with the thumb, and shake. The same result would be obtained by using wood, paper, starch, sugar, or any form of animal or vegetable matter.

Connect a piece of pipe-stem with the rubber tube of your Bunsen burner. Turn on the gas gently and light the jet. Turn down the gas so as to get a flame about half an inch long. Then insert it into a flask placed horizontally and containing only air. Allow it to burn as long as it will. Then turn off the gas; pour into the flask some lime-water, and shake. Wood, paper, or any form of animal or vegetable matter that burns in the air could be employed in this experiment instead of illuminating-gas. What evidence have you had in the past that illuminating-gas contains hydrogen?

Another Oxide of Carbon.—Take a piece of hard-glass tubing about six inches long and one quarter of an inch inside diameter. Loosely fill the middle four inches of it with *coarse* charcoal powder. Connect one end by means of a sleeve-joint with a small flask containing marble and dilute hydrochloric acid, to give a *slow* stream of carbonic dioxide. To the other end attach in the same way a delivery-tube dipping under the surface of a little strong potassic hydroxide solution in a small crystallizing-dish. Fill a test-tube with the same solution and invert it in the crystallizing-dish. This solution, it will be remembered, absorbs carbonic dioxide eagerly. Heat the charcoal as hot as possible with the flame while the current of carbonic dioxide is passing over it. When the test-tube has filled up, remove it and bring a light near the mouth of it. Note the odor of the gas. Is it familiar? What is formed when the gas burns? To settle this, make second test-tube of it, and transfer it under water to another test-tube. Turn this test-tube mouth upward and light the gas. When it ceases burning, pour in lime-water and shake. What seems to be the relation between these two oxides?

Decomposition of Carbonic Dioxide by Metallic Sodium.—Fill a jar with carbonic dioxide by simply allowing the heavy gas to flow into it from the little generator used in the last experiment. Heat a piece of sodium in your iron spoon until it takes fire. Then plunge the spoon down into the jar. What evidence have you that the gas is decomposed?

Effect of Hot Carbon upon Metallic Oxides.—Into your small hard-glass tube sealed at one end put a carefully ground mixture of 1.5 grams of cupric oxide and 0.2 of a gram of powdered charcoal. Arrange a delivery-tube dipping under lime-water in a test-tube. Heat the mixture as hot as possible with the lamp for some time. Examine the contents of the tube. What appears to have taken place? What gas has been evolved?

LECTURE 61.

CARBON AND ITS COMPOUNDS

THE element carbon is, as we have seen, noteworthy on account of the number and variety of its compounds, and the very important part these play in the economy of nature. The element itself is, however, a very remarkable and interesting substance. In the first place, it occurs in three perfectly well defined modifications. We have met with such cases several times before in our study, but nowhere are the apparent differences between the modifications so pronounced as here; on the other hand, there is no case where there is clearer and more unmistakable evidence that these apparently different substances are one and the same thing. We will now briefly consider these three *allotropic* forms of carbon in turn.

1. *Charcoal, Coke, Lampblack.* — Although these substances have different origins, they are too much alike to separate. They result when compounds rich in carbon, such as wood, starch, sugar, soft coal, waxes, oils, etc., are heated to a high temperature out of contact with the air. We will now see how these conditions are met in the every-day production of these substances.

Wood is composed mainly of very complex compounds of carbon, hydrogen, and oxygen. When a piece of wood is heated, the first thing that takes place is a partial breaking down of these complex compounds. The products of this decomposition may be roughly divided into *volatile products*, comprising liquids and gases, mostly inflammable; and *non-*

volatile products, consisting chiefly of carbon, but containing also potassium, calcium, iron, aluminum, silica, etc., compounds of which enter into the composition of all forms of vegetable growth. If the heating takes place in the open air or in oxygen, and if the temperature be steadily raised, some one of the gaseous products will soon take fire and burn; this in turn will raise the temperature of the carbon high enough to set it burning, so that the whole of the oxidizable portion of the wood will in time be consumed. If, however, the heating of the wood be conducted out of contact with air or oxygen, the decomposition goes on until there remains simply a black mass of unburned carbon, which usually retains perfectly the structural appearance of the wood.

Carbon in this form is called *charcoal*. It has been of great value in times past as a fuel, and it is still used quite extensively under particular circumstances.

In practice charcoal is made by stacking billets of wood on end close together, one tier on another, until the pile is of the size desired. Finally the whole pile is covered with turf and lighted at several points round the base, where openings are left for the purpose. The general result is that part of the wood is consumed, and heat enough is thus generated to decompose the rest. In order to secure good results the pile must be carefully watched and skilfully managed. If the temperature rises too high, some of the openings must be stopped. Sometimes a pile suddenly bursts out into flame and the whole lot is lost. The quantity of charcoal actually obtained varies considerably. On the average the yield is about one fourth the weight of wood taken. The woods most commonly used are willow and poplar.

Charcoal commonly floats on water, but this is because it is very porous and is buoyed up by the air in its pores. In powder form it sinks.

It absorbs most gases, some in very large quantities. For example, it absorbs something like one hundred times its volume of ammonia gas and fifty times its volume of carbonic dioxide, though charcoal from different woods shows different degrees of power in this direction. Pans of hot charcoal are used to absorb disagreeable-smelling gases, and filters of powdered charcoal, when judiciously used and *frequently renewed*, have a certain usefulness in purifying water.

Powdered charcoal is occasionally used in medicine, sometimes externally as a sort of poultice for ulcers and other forms of sores, and sometimes internally.

Bone-charcoal, or *bone-black*, which is made by heating bones to a high temperature out of contact with air, is especially interesting, on account of its power to remove the coloring matter from solutions. It is used for this purpose in the laboratory, but the largest quantities are used in the sugar-refineries for decolorizing the syrup.

Charcoal, when freed from the impurities it ordinarily contains, is, so far as measurement can show, perfectly insoluble in all ordinary liquids. It is also entirely unacted upon by the air, or by any element or compound whatever at ordinary temperatures. At a dull red heat it unites with oxygen, and at higher temperatures with chlorine, sulphur, nitrogen, hydrogen, and other elements. At very high temperatures it forms with the metals compounds called *carbides*, which have not been very extensively studied.

Charcoal knows no decay. The only change it can undergo, even when exposed to the weather for years, is a gradual disintegration caused by the mechanical (not chemical) action of the one agent to which all solid forms of matter must sooner or later yield—*water*. Water, collecting in the pores, freezes in the winter ; and the ice expanding as it forms tears the fibres apart, and in time disintegrates the whole mass, as it does the hardest rocks. This action of water is impressive. If the earth endures long enough, the highest mountains will be brought down to the general level by the slow and insidious action of this wonderful substance.

Coke is obtained from soft (or bituminous) coal in the same way that charcoal is obtained from wood. Some is obtained as a by-product at the gas-works, where soft coal is heated for the purpose of making illuminating-gas. Some is made for use as a fuel, by heating the coal in huge ovens. In this case no care is taken, as a rule, to save the gaseous products. Coke is a gray, shining, brittle, compact substance, which generally rings slightly when struck. When used as a fuel it burns a little more rapidly than hard coal and with a clear blue flame. It makes a hot, clean fire. Like charcoal it resists the action of all solvents and reagents at ordinary temperatures.

Lampblack is usually obtained by the burning of tallow or oils. When these are heated in the air the same thing happens as in the case of wood. The material is decomposed and gaseous products rich in carbon are formed which take fire and burn with a bright yellow flame. This flame, or any other, consists mainly of burning gas. The yellow color in this case is due to the fact that it is only in the outer portion of the flame, where there is plenty of oxygen, that complete burning takes place. In the interior the gases are more or less broken down by the heat, with separation of carbon in the form of very small particles, which, being heated to a high temperature, glow and give the flame its lighting power. If such a flame be allowed to strike upon a cold surface, the particles are deposited as a fine jet-black powdery substance, which is mainly carbon. Lampblack is used mixed with shellac or oil as a "dead-black" paint. It is also the main ingredient of printer's ink.

The common Bunsen lamp is a device by which illuminating-gas can be made to burn with a *non-luminous* flame, that is, without any unburned carbon being present in the flame at any time. This is accomplished by causing the gas to mix with air which is drawn in through holes at the base of the burner. The result is that the air and gas come to the mouth of the burner ready mixed, and there is oxygen enough present in the interior of the flame to burn all the carbon. When the base holes are closed the flame becomes luminous. The faint blue color of the ordinary Bunsen flame is simply due to the colored light which the hot gases, or mixture of gases, give out at high temperatures; and the different color of the little inner cone of the flame is determined partly by the difference in temperature and partly by the difference in the character of the gas mixture.

The next modification of carbon to be considered is *graphite* (sometimes called *plumbago* or *black lead*). This is a soft, gray substance, looking much like coke, and occurring in nature in considerable quantities. It gives a gray streak when drawn across paper, and is used in the manufacture of pencils. It is harder to burn than any of the forms of carbon we have noted thus far. It is found in cast iron in the form of semi-crystalline scales, and its presence there is due to the fact that molten iron dissolves carbon at high temperatures. On cooling under ordinary conditions some of the carbon crystallizes out, while some remains united with iron and other elements. When the iron is cooled very slowly and under great pressure microscopic crystals are obtained which are identical in all respects with *the diamond*, which is the last and most remarkable form of the element carbon.

It is found mainly in South America (Brazil) and South Africa. Very small crystals have been found in some meteorites. It is generally colorless. Sometimes the natural crystals are nearly perfect octahedra, but a great deal of what is found consists of imperfect or broken crystals. It is usually found enclosed in nodules of a certain kind of brownish rock. The diamond is almost the hardest substance known. It refracts light powerfully, and its surfaces when cut and polished are very brilliant. It is the most prized of all gems. It can be transformed *without loss of weight* into graphite by heating to a high temperature out of contact with the air. Heated to a high temperature in oxygen it burns, forming carbonic dioxide. It was stated above that microscopic diamonds had been made by crystallizing carbon from iron slowly at high pressures. This and other facts seem to indicate that it has been formed by a similar process in nature.

That these three forms of carbon are all the same is shown sufficiently by the fact that equal weights of the three burn completely in oxygen with the formation of equal weights of carbonic dioxide, *nothing else being formed.* We have no means of knowing to what the physical differences between them may be due.

COMPOUNDS OF CARBON.

Oxides.—When carbon is burned in a limited supply of air, or when carbonic dioxide is passed over red-hot charcoal or coal, there is formed an inflammable gas of peculiar odor, which burns forming carbonic dioxide. Analysis shows that its formula is CO, and it is called *carbon monoxide*, or *carbonic oxide.* It is formed in hard-coal stoves, and the blue flame playing over the surface of such a fire is due to the burning of this gas. Commercially it is important, being one of the main constituents of the so-called *water-gas*, which is made by passing steam over red-hot coal, the resulting gas being a mixture of hydrogen and carbonic oxide. It is very poisonous, and any considerable dose results in almost instant insensibility, death speedily following unless prompt measures be taken. The first requisite is plenty of fresh air, and cold water applied to the head, face, and neck. If breathing shows signs of slackening, it must be kept up by artificial means, as in drowning cases.

Carbonic oxide is sparingly soluble in water. Its solution is not acid. When, however, it is passed over solid potassic hydroxide at 100° the two substances unite directly, forming a substance of the formula $HKCO_2$. By treating this with dilute sulphuric acid and distilling we obtain an aqueous solution of an acid of the formula H_2CO_2, which is called *formic acid*, because the same substance is found in the bodies of ants. In old times the Norwegian peasants used to stew red ants with water and strain off the weakly acid liquid, which was then used under the name of *ant vinegar*, as a substitute for ordinary vinegar, which consists mainly of acetic acid.

Carbonic Dioxide.—This gas is formed when carbon burns in an abundant supply of air or oxygen. It is also one of the final products formed when animal or vegetable substances are burned in air or oxygen, or when they decay in contact with the air. We have already had considerable to do with its chemistry, and our attention will now be devoted to some of its relations to organized life on the earth.

We have already seen that it is formed in the lungs of animals during the act of respiration. It is also evolved by plants, though not to such a conspicuous extent. It follows that enormous quantities are constantly being produced by living organisms as well as in all forms of burning, and in the expulsion of carbonic dioxide from carbonates, such as limestone (in the manufacture of lime).

With this in mind it seems a trifle curious, at first sight, that the quantity of carbonic dioxide in the atmosphere is only about 3 cubic centimeters in 10 liters, and that this small proportion has remained practically constant ever since analyses have been made. When, however, we consider that the gas is the food of every tree and shrub it does not seem so strange. Moreover, the gas is constantly being dissolved by natural waters, and carried away under the surface of the earth, where it becomes fixed in the form of metallic carbonates. It is a simple matter of balance between income and outgo.

There is good reason to believe that in past geological ages the atmosphere was richer in carbonic dioxide than it is at present. Vegetation flourished under the circumstances, and as the proportion of animal to vegetable life was less than now the result was that carbonic dioxide was used faster than it was returned, and the supply slowly diminished, the supply of oxygen in the air increasing proportionally until finally the conditions came down to their present state. The massive forests, representing great storehouses of carbon, abstracted from the atmospheric carbonic dioxide, were in the course of time overthrown and submerged, first by water, afterward by sediments, and thus began the series of processes which have resulted in the immense coal-beds which we are now slowly transforming back into carbonic dioxide in our stoves and furnaces.

Carbonic dioxide is 1.53 times as heavy as air. It dissolves in its own volume of pure water at ordinary temperatures. It does not support ordinary burning, but some of the metals will burn in it when the burning is once started, notably sodium, potassium, and magnesium. Animals cannot live in an atmosphere of carbonic dioxide, but it is a disputed question to-day whether the gas acts upon the system as a real poison, or whether it simply suffocates. Most of the experimental data seem to point to the latter conclusion.

When the gas is dissolved in water under pressure, a solution is obtained which colors blue litmus wine red and is believed to contain *carbonic acid.* Common "soda-water" is such a solution. When the pressure is released there is a violent evolution of carbonic dioxide and there remains a very dilute solution. We have seen the important part this fact plays in the behavior of carbonates toward acids.

Compounds of carbon and hydrogen make up practically the whole of *petroleum oil.* The substances known as *naphtha*, *gasoline*, *benzine*, *kerosene*, *vaseline*, and *paraffin*, together with many of the lubricating-oils used in the cylinders and bearings of steam-engines, are all mixtures of carbon-hydrogen compounds, or *hydrocarbons* as they are called. Many of these compounds have been isolated and analyzed. The simplest naturally occurring compound of carbon and hydrogen has the formula CH_4. It is called marsh-gas, because it may be obtained by stirring up the mud of stagnant ponds, when a light, inflammable gas rises to the surface in bubbles. It also issues from the seams of coal-beds and collects in mines, where it becomes a great element of danger, since its mixture with air is very explosive. It is responsible for many fatal accidents.

The petroleum hydrocarbons grow gradually in complexity as we pass from the gases and light liquids to the heavy oils, waxes, and paraffins.

When we begin to study their chemistry we find a new and remarkable field opening to us; for we have all the features of inorganic chemistry reproduced in a whole army of acids, bases, salts, and other compounds, in which *groups of atoms* play the part of elements. For example, common alcohol is a good representative of a great class of substances all of which are called alcohols, and all of which are known to be *hydroxides*, not of metals, but of hydrocarbon groups. The formula of common alcohol is C_2H_5OH, and the evidence is that we can, by means of the phosphorus pentachloride reaction, remove an oxygen and a hydrogen atom together, and replace the two by one chlorine atom, or, conversely, we can obtain, by other reactions, a compound having the formula C_2H_5Cl, which, by boiling with water, is transformed into ordinary alcohol, chlorine having gone out and an oxygen and a hydrogen atom having entered the molecule (see under Phosphorus). Alcohol is obtained by the action of a certain ferment upon dilute sugar solutions, from which the alcohol is subsequently distilled off. It is somewhat lighter than water and has an agreeable odor. The commercial article is never pure, but usually contains at least 10% water. By careful redistillation the amount of water may be reduced to about 2%, and this can be removed by adding lime, which unites with the water to form calcic hydroxide, the alcohol remaining untouched.

The uses of alcohol are very numerous. It is used to dissolve shellac and other resins and gums to make the "spirit varnishes." It hardens animal tissues and acts as a poison toward most animal and vegetable organisms. Both these facts make it a valuable preservative for zoological specimens. It is occasionally of great value in medicine, since it acts as a stimulant. In emergencies where prompt stimulating action is demanded it is indispensable. On account of its low freezing-point (—130.5°) it is used instead of mercury in thermometers intended for measuring low temperatures. The alcoholic beverages, wine, beer, brandy, whisky, rum, etc., are essentially mixtures of water and alcohol. Some of the stronger liquors (brandy for example) contain small quantities of other substances which are added to give special color or flavor. Beers contain from 2 to 8 per cent alcohol; wines contain from 8 to 17 per cent; brandy, whisky, and rum contain from 40 to 50 per cent.

There is another alcohol which has some commercial importance. It is called *wood-alcohol* or *wood-spirit.* It is found among the products obtained by carefully heating wood in large iron retorts and condensing the vapors that come over.

The liquid thus obtained contains about one per cent of this alcohol. It boils at. 66° and has a rather rank smoky odor even when fairly pure. Its formula is known to be CH_3OH, and the evidence is of the same character as in the case of ordinary alcohol. It can be used for many of the purposes for which common alcohol is used, but it is poisonous, and hence cannot be used in beverages.

Ether is a representative of a class of substances which are known to be oxides of the same groups of which the alcohols are hydroxides. Its formula is known to be

$(C_2H_5)_2O$. It is a very inflammable liquid with a low boiling-point (34.5°) and a heavy vapor which forms a dangerously explosive mixture with air. It is made by heating alcohol with sulphuric acid under carefully regulated conditions. The process is a rather dangerous one at best. Ether is used to produce insensibility to pain in surgical operations; but it is also a valuable solvent and has many uses in the organic laboratory.

Acetic acid is a good representative of the organic acids. It is obtained (1) by the action of the *acetous ferment* upon sugar solutions; (2) by the action of the same ferment upon dilute alcohol; (3) by the action of liquid oxidizing mixtures upon common alcohol; (4) by the dry distillation of wood. The crude acid from this latter source is called *pyroligneous acid.* Most "vinegar" is made by the first two processes. Purer and stronger acetic acid is made from products obtained by the last two. The formula of the acid is $C_2H_4O_2$ or $H(C_2H_3O_2)$. It has only one replaceable hydrogen, and this is known to be united with oxygen in an hydroxyl group. Its salts are called *acetates.*

The only other organic substances to be mentioned are a few from a class known as the *carbohydrates*, which includes starch and the sugars.

Starch is a compound of carbon, hydrogen, and oxygen. Its exact formula is not known, as there is no way of getting at its molecular weight, it being non-volatile and insoluble in most liquids: but it is some multiple of $C_6H_{10}O_5$. It is found in the seeds, roots, and stems of plants, such as wheat, corn, potatoes, and arrowroot. It is separated by crushing the material in contact with water and draining off the liquid through a sieve or through bolting-cloth. The milky filtrate is allowed to stand, when the starch settles as a white powder, which the microscope shows to consist of minute rounded granules.

Grape-sugar (glucose or dextrose, $C_6H_{12}O_6$) is present in grape-juice and in honey. It can be made by boiling starch with dilute sulphuric acid. The acid is unchanged at the end of the operation and can be neutralized with chalk. Grape-sugar is not so sweet as cane-sugar. It acts upon alkaline silver and copper solutions as a reducer (see under Silver and Copper).

Cane-sugar, $C_{12}H_{22}O_{11}$, is obtained from sugar-cane and from the beet-root. It is present in many fruits. When boiled with dilute acids it is transformed into sugars of the formula $C_6H_{12}O_6$ (like dextrose).

LECTURE 62.

CONCLUSION.

THE chemistry of the carbon compounds brings us face to face with some of the most impressive facts in all physical science. To be sure some of these facts crop out everywhere, but here they force themselves upon our notice. As a vantage-point from which to take a final survey of the country we have been travelling, let us consider the relations between carbonic dioxide and life. Plants act upon moist carbonic dioxide in sunlight in such a way that a body closely allied to starch is built up and used by the plant as a food. Oxygen is liberated in the process. Now the two compounds (carbonic dioxide and water) involved in the above synthesis of starch are both substances which are not easily decomposed. To decompose them by heat alone requires an enormously high temperature. In the language of physics it requires the expenditure of considerable *energy* in some form or other. Moreover, when either of these substances is formed from its elements a great deal of energy is liberated in the form of heat. We interpret this as meaning that the elements contain more energy than the compounds formed, in the cases we are considering. In order, then, to pass back from the compound to the elements we must restore the energy which was given out as heat when the union took place.

In the starch formation above mentioned, carbonic dioxide and water are both (partially at least) decomposed. Whence comes the energy? Since the action takes place only in sunlight, we are constrained to answer that it must come from the sun, and that the energy which we in our laboratories can only supply by intense heat, or by some application of energy on an equally heroic scale, is here accomplished with no such *visible* expenditure. All we see is simply a green leaf waving in the sunlight.

Plants form directly or indirectly the food of most animals; and just as the tissues of the plant are built up from the carbonic dioxide they use, so the tissues of animals are built up from the carbon compounds contained in their food; thus the energy given out by the sun becomes stored up in the life-structures of plants and animals. We have already seen how, when plants and animals die, the carbon they contain passes gradually back into carbonic dioxide again and once more begins a new round of activities at the leaf of some plant. The process of decay or decomposition is then mainly one of oxidation; but the oxidation of a given weight of any substance develops the same quantity of heat, no matter whether the substance is oxidized slowly or rapidly; and this brings us to the final point.

Careful study of chemical changes shows that in most of those we see going on around us energy is liberated in the form of heat. Almost every reaction we have performed in the laboratory has been attended with some rise in temperature, and the point is that, so far as can now be seen, the energy thus given out as heat is simply *dissipated*, and only acts to raise by an infinitesimal amount the temperature of the universe. Moreover, it is true that in such cases the greater part of the chemical energy of the original substance is converted into heat and dissipated. If now we look about us to see if we can discover agencies by which heat is being converted back into available energy again on a corresponding scale, we fail to find them. Here, then, we have at last come to a place where income and outgo do not balance. And when we look at the facts from this point of view, and when we let our imaginations run far beyond our own blazing sun to depths of space where blaze thousands of others like it, dissipating energy in the form of heat at a rate beyond all human power of conception, we begin to realize the great fundamental fact of modern physical science, namely, that the universe of which our solar system forms only an infinitesimal part is in just the position of a great clock that is slowly running down, or of a great lake slowly draining itself into the ocean.

As surely as the present order of events continues there must and will come a time, in the course of countless ages, when all the forms of energy we know now will be converted into heat. Moreover, heat tends to diffuse itself by conduction and radiation, and to bring all matter ultimately to the same temperature; under which circumstances there would be an end of all physical phenomena. The transformations of energy which underlie all the phenomena of animate and inanimate nature as we now know it would be no longer possible, just as all possibility of "water power" would vanish if all the water on the earth's surface were brought down to the sea level with no possibility of lifting and distributing it again. At present we realize and utilize a little of the energy of this great machine, but it has in it nothing of permanence and must in time run down and cease its operations forever.

We return once more, then, to the word which might almost be called the keynote of this book, *equilibrium*. All the cases we have studied have depended for their existence upon energy transformations, and the equilibrium has been between two such transformations in opposite directions. Such cases are possible now, while energy exists in so many forms, but the equilibrium toward which all existing things are tending is of a totally different character. It is a *static*, not a dynamic, one—a state of absolute and eternal stagnation.

APPENDIX.

THE MANIPULATION OF GLASS IN THE LABORATORY.

For setting up apparatus it is essential that the student shall be able to bend glass tubing correctly and to seal up ignition-tubes.

The directions usually given for bending glass tubing call for a fish-tail burner: this is not necessary, however. It is perfectly easy with very little practice to bend tubes in a good Bunsen flame, and it is better to start by doing so from the start. In working with the blast-lamp the glass-blower never thinks of resorting to a fish-tail burner every time he wishes to make a bend.

The piece of tubing should be held across the flame (well above the inner cone) and continually turned, until it can be bent by gentle pressure. It should then be bent *very slightly*. It is now reheated, not in the same spot as before, but a very little to one side, turning it all the time, when it can soon be bent a little more, and so on. The knack is easily acquired and the bends are thoroughly good ones.

The art of sealing a piece of hard glass tubing at one end in such a way that it can be heated up without fear of its cracking is a trifle more elusive, but can be gained by a little practice.

First the tubing is heated in the Bunsen flame (or, better, in the blast-lamp flame), with constant turning, until it is so soft that it can be drawn out as shown in Fig. 1. To finish the sealing, the tube is placed in the flame in the position shown in Fig. 2, and the left-hand portion is constantly rotated while the right-hand portion is slowly and steadily drawn off *without turning*. The final result should be as seen in Fig. 3.

All tubes which are to be used in setting up apparatus should be *fire-polished*. To do this the end of the tube is held in the flame and turned until the sharp edges melt and are rounded.

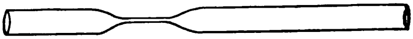


FIG. 1.

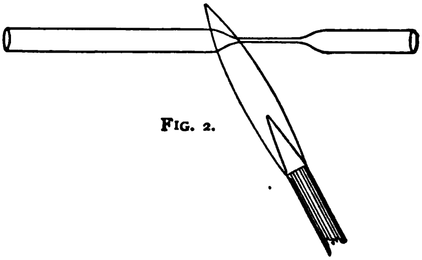


FIG. 2.

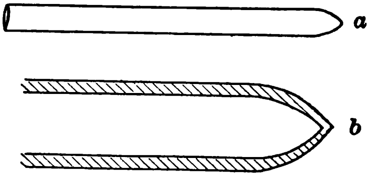


FIG. 3.

There is usually considerable waste glass available in a laboratory, and students should practise on this until they can bend and seal up tubes rapidly and neatly before they undertake to set up any apparatus.

USE OF THE TABLE SHOWING TENSION OF AQUEOUS VAPOR.

The temperature of the gas is to be taken. Suppose it is 19°. This temperature comes between 18.2 and 19.1.

(See left-hand colomn of the table.) Accordingly subtract from the barometer pressure 1.6 cm. or 16 mm. and this gives the corrected barometer pressure.

TABLE OF ATOMIC WEIGHTS.

When two values are given the first is the most accurate value at present known, while the second (in parenthesis) is an approximate value for use in ordinary calculations. The logarithms given are the logarithms of these simple numbers.

APPARATUS REQUIRED.

The following list of apparatus has been found adequate for the work described in the foregoing pages. Articles enclosed in brackets are not essential. The glass tubing needs a little explanation. The "combustion-tubing" is about ½ an inch internal diameter. It would be better to give it out in the form of a single piece about 6 inches long, drawn off and sealed at one end ready for use. The small hard-glass tubing should be about ¼ of an inch internal diameter. The soft-glass tubing should be about ⅛ of an inch internal diameter. I would advise adding a half-ounce bottle filled with shot, for use in counterpoising.

Retort-stand, 2 rings.
Clamp.
Tripod.
Square asbestos-paper.
  " iron netting.
Lamp with hose.
Blowpipe.
Tongs.
Round file.
Triangular file.
Iron crucible.
Pipe-stem triangle.
Pneumatic trough.
Platinum wire.
Test-tube rack.
12 Test-tubes.
Flask 250 cc.
  " 100 cc.
  " 50 cc.
2 Flasks (round bottom) 150 cc.
Boilling-flask 100 cc.
Nest of beakers (4).

Nest of breakers (3).
Wide-mouth bottle 125 cc.
3 Watch-glasses, 2 in.
2 Crystallizing-dishes, 3 in.
Retort 100 cc.
Funnel 2½ in.
  " 4 in.
Funnel-tube.
2 U tubes.
Glass rod.
2 Lengths glass tubing.
Combustion-tube 2 ft.
Small hard-glass tubing 2 ft.
[Suction-pump.]
Thermometer.
Graduated cylinder 100 cc.
Porcelain dish, No. 1.
  " " " 2.
Porcelain dish No. 5.
  " crucible.
Mortar and pestle, 2 in.
Filter-papers, No. 4.
Sulphur-spoon.
Cylinder.
Tin sheet.
Meter-rule.
Set of weights.
3 ft. Rubber hose, ¼ in.
4 Rubber stoppers, No. 2, 1 hole.
2 " " " 6, 1 "
2 " " " 6, 2 "
1 " " " 7, 2 "
2 Pinch-cocks.
Hand-scales.
Clay pipe.

LIST OF BOOKS FOR A TEACHER'S LIBRARY.

Chemical Theory for Beginners.	Dobbin and Walker.	Macmillan.
The Soil.	F. H. King.	Macmillan.
The Chemistry of Common Life.	J. F. W. Johnston.	Appleton.
Inorganic Chemistry.	G. S. Newth.	Longmans.
Foundations of Analytical Chemistry.	W. Ostwald.	Macmillan.
Physical Chemistry for Beginners.	Van Deventer.	Wiley.
Inorganic Chemistry (*Advanced Course*).	Remsen.	Holt.
General Inorganic Chemistry.	P. C. Freer.	Allyn & Bacon.
The Methods of Glass-blowing.	W. A. Shenstone.	Longmans.
A Short History of Chemistry.	F. P. Venable.	Heath.
The Periodic Law.	F. P. Venable.	Chem. Pub. Co.
Elements of Physical Chemistry.	J. L. R. Morgan.	Wiley.
Chemical Lecture Experiments.	G. S. Newth.	Longmans.
Chemical and Geological Essays.	T. S. Hunt.	Scientific Pub. Co.
Outlines of General Chemistry.	W. Ostwald.	Macmillan.
Solutions.	W. Ostwald.	Macmillan.
Introduction to the Study of Chemistry.	Perkin and Lean.	Macmillan.
The Atomic Theory.	Wurtz.	Appleton.
Organic Chemistry.	Remsen.	Heath.
Organic Chemistry.	Whitely.	Longmans.
Theoretical Chemistry.	Nernst.	Macmillan.
Electro-Chemistry.	Le Blanc.	Macmillan.
The Principles of Chemistry.	D. Mendeléeff.	Longmans.
Treatise on Chemistry.	Roscoe & Schorlemmer.	Appleton.

Table of Common Elements.

NAME.	ATOMIC WEIGHT.	LOG.	SYMBOL.
Aluminum	27.1 (27)	1.4314	Al.
Antimony	120	2.0792	Sb.
Arsenic	75.	1.8751	As.
Barium	137.43 (137.4)	2.1380	Ba.
Bismuth	2.08	2.3181	Bi.
Boron	10.95 (11)	1.0414	B.
Bromine	79.95 (80)	1.9031	Br.
Cadmium	112.3 (112)	2.0492	Cd.
Calcium	40.	1.6021	Ca.
Carbon	12.00	1.0792	C.
Chlorine	35.455 (35.5)	1.5502	Cl.
Chromium	52.14 (52)	1.7160	Cr.
Cobalt	59.	1.7709	Co.
Copper	63.60	1.8035	Cu.
Fluorine	19.05 (19)	1.2788	F.
Hydrogen	1.0075 (1)	0.0000	H.
Iodine	126.85 (127)	2.1038	I.
Iron	56.0	1.7432	Fe.
Lead	206.92 (207)	2.3160	Pb.
Lithium	7.03 (7)	0.8451	Li.
Magnesium	24.36 (24)	1.3802	Mg.
Manganese	55.02 (55)	1.7402	Mn.
Mercury	200.	2.3010	Hg.
Nickel	58.7	1.7686	Ni.
Nitrogen	14.045 (14)	1.1461	N.
Oxygen	16.000	1.2041	O.
Phosphorus	31.0	1.4914	P.
Potassium	39.14 (39)	1.5911	K.
Silicon	28.4	1.4533	Si.
Silver	107.93	2.0331	Ag.
Sodium	23.05 (23)	1.3617	Na.
Strontium	87.68 (88)	1.9445	Sr.
Sulphur	32.065 (32)	1.5051	S.
Tin	119.	2.0755	Sn.
Zinc	65.4	1.8156	Zn.

Weight of Gases at 0° and 76 cm.

GAS.	WEIGHT OF 1 CC.	LOG.
Air	.001293 g.	7.1116 − 10
Carbon dioxide	.901977	7.2960 − 10
Chlorine	.003180	7.5024 − 10
Hydrogen	.0000899	5.9538 − 10
Nitrogen	.001250	7.0969 − 10
Oxygen	.001429	7.1550 − 10

Tension of Aqueous Vapor.

BETWEEN		SUBTRACT	BETWEEN		SUBTRACT
9.0°	10.5°	0.9 cm.	19.2°	20.0°	1.7 cm.
10.6	12.0	1.0	20.1	21.0	1.8
12.1	13.4	1.1	21.1	21.8	1.9
13.5	14.7	1.2	21.9	22.6	2.0
14.8	15.9	1.3	22.7	23.4	2.1
16.0	17.0	1.4	23.5	24.2	2.2
17.1	18.1	1.5	24.3	24.9	2.3
18.2	19.1	1.6	25.0	25.6	2.4

	NUMERICAL VALUE.	LOG.
π	3.14159265 +	0.4971
π^2	9.86960	0.9948
$\frac{1}{4}\pi$	0.7854	9.8951 − 10
$\frac{1}{6}\pi$	0.5236	9.7190 − 10

NOTES ON THE TABLES.

Logarithms shorten the processes of multiplication, division, involution and evolution. To multiply two numbers we take their logarithms from the table and add them: the sum gives the logarithm of the product of the numbers; and the corresponding number can be found from the table. In division we subtract the logarithm of the divisor from that of the dividend. To raise a number to any required power we multiply its logarithm by the index of the power. This gives the logarithm of the required result. In extracting roots we divide the logarithm of the number by the index of the root, thus getting the logarithm of the required root.

The logarithm of any number between 1 and 10 is 0.+ a decimal to be found from the table.

For any number between 10 and 100 it is 1. + a decimal
" " " " 100 " 1000 " " 2. + " "
" " " " 1000 " 10000 " " 3. + " "

The logarithm of a number less than 1 (i.e. a decimal fraction) is — 1. + a decimal if the first figure to the right of the decimal point is a real figure (i.e. not 0). If the first figure is 0, the logarithm is — 2. + a decimal: if the first two figures are ciphers, it is — 3. + a decimal, etc.

The decimal can be found as follows:

Suppose the number is 120.3. This number lies between 100 and 1000: hence its logarithm is 2. + a decimal. To find this decimal, first find the first two figures *of the number* in the column marked N (see table). Run out to the right until you reach the column at the head of which stands the third figure of the number (in this case 0), and we find the four-place decimal .0792, to which must be added a small quantity determined by the size of the fourth figure of the number, as follows: The fourth figure is 3. At the right of each page of the table will be found small columns of correction figures headed by the numbers 1, 2, 3, 4, 5. Find the difference between the approximate logarithm you have found in the table and the next higher one. Find this number in the column marked D; and opposite and under 3 will be found a small number which is to be added to the approximate logarithm. In this case $.0828 - .0792 = 36$. The small number is 11 and the sum is $.0792 + 11 = .0803$. The complete logarithm is then 2.0803.

The required logarithm is, then, 2.0802. If the last figure of the number is more than 5 (say 8), take out the corrections under columns 5 and 3 *or under any other two which when added make 8*. Add this sum to the partial logarithm as before.

Suppose now that we wish to find the number corresponding to a given logarithm, say 2.3268.

Disregard the 2. Find the next lower logarithm in the table (in this case it is .3263). Find the difference between it and your logarithm thus, $.3268 - .3263 = .0005$. Regard this difference as a whole number, annex ciphers and divide by the difference between the two logarithms between which the logarithm in question lies (in this case $.3284 - .3263 = 21$; $5 \div 21 = .24$.) Annex this quotient, *disregarding the decimal point*, to the number corresponding to the lowest of the three logarithms (in this case .3263 is the logarithm and 212 is the number.) Annexing we have 21224, and since the logarithm was 2.3268 the number must be between 100 and 1000 and is accordingly 212.24.

TABLE OF COMMON LOGARITHMS.

Except in the zero-column only the last three figures of every logarithm are given.

The first figure of each logarithm is the same as the first figure in the same line of the zero-column, except where an asterisk appears.

* *Where the last three figures of the logarithm are preceded by an asterisk, the first figure is the same as the first figure in the* NEXT *line of the zero-column.*

The computer will have to find for himself the value of D between successive logarithms; but in the space to the right of the heavy vertical line are given the values of the fractions .1D, .2D, .3D, .4D, and .5D corresponding to each value of D. This is the table of proportional parts.

N	0	1	2	3	4	5	6	7	8	9
10	0000	043	086	128	170	212	253	294	334	374
11	0414	453	492	531	569	607	645	682	719	755
12	0792	828	864	899	934	969	*004	*038	*072	*106
13	1139	173	206	239	271	303	335	367	399	430
14	1461	492	523	553	584	614	644	673	703	732
15	1761	790	818	847	875	903	931	959	987	*014
16	2041	068	095	122	148	175	201	227	253	279
17	2304	330	355	380	405	430	455	480	504	529
18	2553	577	601	625	648	672	695	718	742	765
19	2788	810	833	856	878	900	923	945	967	989
20	3010	032	054	075	096	118	139	160	181	201
21	3222	243	263	284	304	324	345	365	385	404
22	3424	444	464	483	502	522	541	560	579	598
23	3617	636	655	674	692	711	729	747	766	784
24	3802	820	838	856	874	892	909	927	945	962
25	3979	997	*014	*031	*048	*065	*082	*099	*116	*133
26	4150	166	183	200	216	232	249	265	281	298
27	4314	330	346	362	378	393	409	425	440	456
28	4472	487	502	518	533	548	564	579	594	609
29	4624	639	654	669	683	698	713	728	742	757
30	4771	786	800	814	829	843	857	871	886	900
31	4914	928	942	955	969	983	997	*011	*024	*038
32	5051	065	079	092	105	119	132	145	159	172
33	5185	198	211	224	237	250	263	276	289	302
34	5315	328	340	353	366	378	391	403	416	428
35	5441	453	465	478	490	502	514	527	539	551
36	5563	575	587	599	611	623	635	647	658	670
37	5682	694	705	717	729	740	752	763	775	786
38	5798	809	821	832	843	855	866	877	888	899
39	5911	922	933	944	955	966	977	988	999	*010
40	6021	031	042	053	064	075	085	096	107	117
41	6128	138	149	160	170	180	191	201	212	222
42	6232	243	253	263	274	284	294	304	314	325
43	6335	345	355	365	375	385	395	405	415	425
44	6435	444	454	464	474	484	493	503	513	522
45	6532	542	551	561	571	580	590	599	609	618
46	6628	637	646	656	665	675	684	693	702	712
47	6721	730	739	749	758	767	776	785	794	803
48	6812	821	830	839	848	857	866	875	884	893
49	6902	911	920	928	937	946	955	964	972	981
50	6990	998	*007	*016	*024	*033	*042	*050	*059	*067
51	7076	084	093	101	110	118	126	135	143	152
52	7160	168	177	185	193	202	210	218	226	235
53	7243	251	259	267	275	284	292	300	308	316
54	7324	332	340	348	356	364	372	380	388	396

D	1	2	3	4	5
43	4	9	13	17	22
42	4	8	13	17	21
41	4	8	12	16	20
40	4	8	12	16	20
39	4	8	12	16	20
38	4	8	11	15	19
37	4	7	11	15	18
36	4	7	11	14	18
35	4	7	10	14	18
34	3	7	10	14	17
33	3	7	10	13	16
32	3	6	10	13	16
31	3	6	9	12	16
30	3	6	9	12	15
29	3	6	9	12	14
28	3	6	8	11	14
27	3	5	8	11	14
26	3	5	8	10	13
25	2	5	8	10	12
24	2	5	7	10	12
23	2	5	7	9	12
22	2	4	7	9	11
21	2	4	6	8	10
20	2	4	6	8	10
19	2	4	6	8	10
18	2	4	5	7	9
17	2	3	5	7	8
16	2	3	5	6	8
15	2	3	4	6	8
14	1	3	4	6	7
13	1	3	4	5	6
12	1	2	4	5	6
11	1	2	3	4	6
10	1	2	3	4	5
9	1	2	3	4	4
8	1	2	2	3	4

N	0	1	2	3	4	5	6	7	8	9	D	1	2	3	4	5
55	7404	412	419	427	435	443	451	459	466	474	8	1	2	2	3	4
56	7482	490	497	505	513	520	528	536	543	551						
57	7559	566	574	582	589	597	604	612	619	627						
58	7634	642	649	657	664	672	679	686	694	701						
59	7709	716	723	731	738	745	752	760	767	774						
60	7782	789	796	803	810	818	825	832	839	846	7	1	1	2	3	4
61	7853	860	868	875	882	889	896	903	910	917						
62	7924	931	938	945	952	959	966	973	980	987						
63	7993	*000	*007	*014	*021	*028	*035	*041	*048	*055						
64	8062	069	075	082	089	096	102	109	116	122						
65	8129	136	142	149	156	162	169	176	182	189	6	1	1	2	2	3
66	8195	202	209	215	222	228	235	241	248	254						
67	8261	267	274	280	287	293	299	306	312	319						
68	8325	331	338	344	351	357	363	370	376	382						
69	8388	395	401	407	414	420	426	432	439	445						
70	8451	457	463	470	476	482	488	494	500	506						
71	8513	519	525	531	537	543	549	555	561	567						
72	8573	579	585	591	597	603	609	615	621	627						
73	8633	639	645	651	657	663	669	675	681	686						
74	8692	698	704	710	716	722	727	733	739	745						
75	8751	756	762	768	774	779	785	791	797	802						
76	8808	814	820	825	831	837	842	848	854	859						
77	8865	871	876	882	887	893	899	904	910	915						
78	8921	927	932	938	943	949	954	960	965	971						
79	8976	982	987	993	998	*004	*009	*015	*020	*025						
80	9031	036	042	047	053	058	063	069	074	079	5	0	1	2	2	2
81	9085	090	096	101	106	112	117	122	128	133						
82	9138	143	149	154	159	165	170	175	180	186						
83	9191	196	201	206	212	217	222	227	232	238						
84	9243	248	253	258	263	269	274	279	284	289						
85	9294	299	304	309	315	320	325	330	335	340						
86	9345	350	355	360	365	370	375	380	385	390						
87	9395	400	405	410	415	420	425	430	435	440						
88	9445	450	455	460	465	469	474	479	484	489						
89	9494	499	504	509	513	518	523	528	533	538						
90	9542	547	552	557	562	566	571	576	581	586	4	0	1	1	2	2
91	9590	595	600	605	609	614	619	624	628	633						
92	9638	643	647	652	657	661	666	671	675	680						
93	9685	689	694	699	703	708	713	717	722	727						
94	9731	736	741	745	750	754	759	763	768	773						
95	9777	782	786	791	795	800	805	809	814	818						
96	9823	827	832	836	841	845	850	854	859	863						
97	9868	872	877	881	886	890	894	899	903	908						
98	9912	917	921	926	930	934	939	943	948	952						
99	9956	961	965	969	974	978	983	987	991	996						

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